

E-27-605

**FINAL REPORT**

**DYES IN THE ENVIRONMENT: DYEING WASTES IN LANDFILL**

**Prepared By:**

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**Sponsored by:**

**The U.S. Operating Committee of the  
Ecological and Toxicological Association  
of the Dyestuffs Manufacturing Industry**

**March 1988**

**GEORGIA INSTITUTE OF TECHNOLOGY**

**A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA**

**SCHOOL OF TEXTILE ENGINEERING**

**ATLANTA, GEORGIA 30332**



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## Abstract

Experiments have been conducted to determine the fate of dyes that enter landfill via sludge from biological treatment plants receiving textile dyeing wastewater. A simulated landfill facility was constructed and filled with sludges from three treatment plants receiving > 75% textile dyeing wastewater. The landfill facility was maintained for three years and samples of effluent and landfill interior were analyzed for 24 dyes used in large volumes in textile dyeing. Sludge from a plant not receiving dyeing wastewater was used as a control.

The samples were concentrated 100-fold by evaporating 1 liter of effluent and taking up the residue in 10 ml of methanol for acid, direct and reactive dyes and 10 ml of benzene for disperse dyes. The concentrates were analyzed by High Performance Liquid Chromatography. Detectability limits were 1 to 10 parts-per-billion for most of the dyes included in the study.

No dyes were present in the effluents or column interior samples at levels greater than the detectability limits. Subsequent studies on dyes exposed to sludges suggest that the dyes are strongly adsorbed and tenaciously held by wastewater treatment plant sludge.

Effluent and interior samples were also analyzed for priority pollutants and possible dye degradation products by gas chromatography-mass spectrometry. No dye degradation products were found in the dye column effluent samples. Several aromatic amines were present in the dye column interior sample. None of these amines, except possibly aniline, could have been produced by degradation of the dyes in this study.

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## I. Introduction

Wastes produced as a result of dye manufacturing and textile dyeing processes continue to be a concern of government agencies responsible for environmental regulation. At least part of this concern stems from the scarcity of published information on the fate of the dyes in the environment.

Wastewater from textile dyeing operations is usually biologically treated by the activated sludge process operating in the extended aeration mode. This process is very effective in removal of many textile processing chemicals contributing to the biochemical oxygen demand of the wastewater but many dyes are resistant to degradation in this process. Dyes usually leave such a treatment facility either in the clarifier effluent or as part of the sludge that is wasted from the treatment plant.

Earlier publications (1-3) have reported results of studies on dye concentrations in clarifier effluent from waste treatment plants receiving large volumes of textile processing wastewater. These studies suggest that some dyes are removed from the wastewater in the activated sludge process but it was not clear whether dye degradation or adsorption on sludge was the removal mechanism. This aspect of the fate of dyes in the environment is currently under study by other investigators (4).

No work has been reported in the literature on the fate of dyes removed from wastewater treatment plants on sludge. Waste sludge is usually subjected to some type of thickening process (centrifugation, sand drying, mechanical thickening, etc.) and the solids placed in landfill. Under landfill conditions dyestuffs would be subjected for long periods of time to anaerobic conditions and to leaching. Either the dyestuffs themselves or the degradation products might be leached from the landfill and contaminate surface or ground water.

The objectives of the present work were:

1. To determine if selected dyestuffs are leached from sludges removed from textile wastewater treatment plants.



2. To determine if expected dye degradation products are detectable in landfill leachates.

To accomplish the objectives a simulated landfill facility was constructed and filled with sludges from textile dyeing wastewater treatment plants. Leachates were collected over a period of 3 years and analyzed for dyes and dye degradation products.

## II. Simulated Landfill Facility

A simulated landfill facility was constructed from two sections of six-foot long, 2-1/2 feet in diameter fused clay pipe. The two sections were placed end-to-end vertically to give a 12-foot tall unit. Three units were originally constructed but only two were used in the study. The pipes were constructed on a welded steel frame and set in concrete with a conical drain at the bottom of each pipe. A diagram of the facility is shown in Figure 1. These columns were erected in a large laboratory in the School of Textile Engineering building at Georgia Tech. A cross-section of the column is shown in Figure 2.

The bottom of each column was filled with 2 inches of coarse gravel followed by 2 inches of fine gravel and topped with 2 inches of sand. A 2-foot layer of typical clay soil was placed in the bottom of the column to simulate the type of clay soil used in landfill construction. This soil was obtained from a construction site on the Georgia Tech campus. All soil placed in the columns was sieved through a 1/2" metal screen to remove rocks and other debris. The remainder of the column was filled with alternating layers of waste sludge (2 feet) and clay soil (6 inches) to simulate fill and cover procedures used in landfill construction. The top of the column was covered with a 2 foot layer of top soil obtained at the same construction site.

## III. Column Filling

Three wastewater treatment plants were selected for sludge collection. These plants were coded A, B and C. All plants selected for study treated an influent containing at least 75%

wastewater from textile dyeing and finishing processes. This ensured that the wastewater treatment plant had a high concentration of dyestuffs of interest in the study. All three plants were activated sludge systems operated in extended aeration mode. All three plants were reported to be operated efficiently and to represent current state-of-the-art in textile wastewater treatment.

Plant A is a municipal system typically processing 35 million gallons per day of wastewater. Approximately 90% of the wastewater is from industrial sources. The plant achieves 97-98% BOD reduction. Sludge obtained from this plant had been sand bed dried. Most of the industrial wastewater treated in this plant is effluent from carpet dyeing operations with primarily acid dyes. Textile dyeing operations discharging to Plant A use approximately 600,000 pounds of dyes per month.

Plant B is operated by a textile company and has a capacity of 2 million gallons per day. The influent is almost 100% textile process wastewater. The plant processes waste from desizing, scouring, bleaching, continuous dyeing and printing operations. The fabric processed is polyester-cotton blends for both home furnishing and apparel end uses. The plant uses large volumes of vat, disperse, and sulfur dyes. In addition to dyes the plant uses large quantities of salt, hydrogen peroxide, sodium hydroxide, and surfactants. The effluent pH was approximately 12 with an influent BOD of 900-1000 ppm. The dyeing operations discharging to Plant B use approximately 60,000 pounds of dyestuffs per month.

Plant C is a municipal plant processing 1.5 million gallons of wastewater per day with 75% of the influent from textile dyeing processes. Plant C achieves a 98% BOD removal with a 5-day residence time. One textile operation discharging to Plant C is a yarn dyeing operation (polyester-cotton blend) using reactive and disperse dyes. A second textile operation discharging to Plant C dyes polyester and polyester-cotton blend apparel fabrics primarily for ladies wear. Direct, reactive, and disperse dyes are used in dyeing at this textile plant. The yarn

dyeing plant uses almost 8,500 pounds of dye per month and the fabric plant about 20,000 pounds of dye per month.

Sludge was collected from the three wastewater treatment plants in the form that would normally be sent to landfill. Plants A and C use sand bed drying to dewater sludge but Plant B used a mechanical thickening process. Sludges were collected from all three plants in cleaned 55-gallon drums.

The percent dry solids of all three sludges were obtained gravimetrically. A weighed sample of each sludge was placed in a vacuum oven at 150°C and heated under vacuum until a constant weight was achieved. The percent solids was significantly different for the three sludge samples as shown below:

Sludge Plant A	97.1% solids
Sludge Plant B	9.2% solids
Sludge Plant C	23.2% solids

The sludge from Plant A was unusually high in solids. From examination of the sludge from Plant A, it was obvious that it contained a very high percentage (> 50%) of fibers. This fiber (nylon) has a relatively low moisture regain and would have permitted the sludge to drain more readily in sand bed drying than would be the case with typical wastewater treatment plant sludge. In order to achieve approximately equal weight of dry sludge, a weight ratio of 1:10:4 (Plant A: Plant B: Plant C) was used in mixing sludges for column filling.

The three sludges were mixed in the ratios shown above in 150 pound lots by adding the appropriate weight of each sludge and mixing in a 55-gallon drum. The 150 pound lot was then placed in the column and the next batch mixed. The bottom layer of sludge in the simulated landfill contained 450 pounds of sludge and the middle and top layers contained 525 pounds of sludge for a total of 1500 pounds of sludge. The 3 layers were separated by a 6" layer of clay soil (see Figure 2). This column was designed as the "Dye Column".

A Control Column was also prepared for comparison with the Dye Column. Sludge for the Control Column was obtained from a wastewater treatment plant in the Atlanta area known to be

treating domestic waste free of industrial wastewater. The sand bed dewatered sludge was packed in the control column in the same manner as sludge in the Dye Column. Because the control sludge was quite dry only 1030 pounds could be placed in the control column (330 pounds in the bottom layer, 350 pounds in the middle layer and 350 pounds in the top layer).

Samples of each of the sludges individually and samples of the mixed dye column sludge were placed in clean freezer jars and frozen. These retained sludge samples were used for sludge analysis.

Both columns were wrapped with glass fiber insulation to retain heat. Both columns were fitted with a device to permit sampling of the water in the column interior and a probe to permit monitoring of the column temperature.

Due to the slow rate of percolation of water through the columns, a layer of water was always present on top of the columns. Significant gas evolution could be observed as bubbles coming to the surface of the water and a strong hydrocarbon like odor was present at the top of the columns. These observations suggest that anaerobic conditions were present in the column interiors.

After 3 years the level of solid material in the columns had dropped by approximately 1.5 feet. This may have been due to compaction of the solid material or to actual decomposition of the sludge. Since the column had been very carefully packed and the drop in level of solids was gradual over the 3 year period, the latter explanation seems more probable.

The columns were filled in late December of 1983. Within 15 days the interior temperature had risen to 70.5 F and essentially stabilized at that temperature.

Average rainfall for the Atlanta area was obtained from the National Weather Service. The 30-year average through 1982 was 48.29 inches per year. Thus, a 27-inch in diameter column would require 120 gallons of water per year. Distilled water was added to both columns in a regular basis to achieve this level of water addition. Water addition continued for the three years that the

columns were maintained.

#### IV. Sample Collection

Effluents were collected from the columns on a regular basis. Upon collection from the column the effluents were placed in clean freezer jars and maintained in a freezer until analyzed.

An unexpected problem developed in that very little effluent was obtained from the columns. The original plan was to analyze the effluent at the end of one year (i.e. early in 1985) but sufficient effluent was not available to conduct the analysis at that time. It was not until late in 1986 (3 years later) that enough effluent was collected to conduct the analytical phase of the work. Apparently the clay soil layer served as a very effective barrier to the percolation of water to the collection system at the base of the columns.

Late in 1986 samples of the dye and control column interiors were collected for analysis. Due to a failure of the sampling device in the Control Column, insufficient sample was obtained for analysis. However, no problems were experienced in obtaining a sample of the dye column interior.

Thus, after a 3 year period the following samples were available for analysis:

- Dye Column Retained Sludge
- Dye Column Effluent
- Dye Column Interior
- Control Column Effluent

These samples were subjected to analysis for both dyes and probable dye degradation products.

#### V. Dyes Selected for Study

Two criteria were used in selection of dyes for the study. First the selected dyes must be used in large volume in textile dyeing operation. Second, the dyes must be used in large volumes by textile dyeing operations discharging to the three wastewater treatment plants selected for sludge collection. Inventory

records of the textile plants discharging to the selected wastewater treatment facilities were reviewed and showed that the dyes selected for study were being used in large volume at the time the study was conducted. The initial list of 28 dyes selected for study is given in Table 1. During the course of purification and analytical method development, some dyes had to be removed from the selected list because of unforeseen problems. Reactive Blue 21 differs greatly in structure from the other dyes and could not be analyzed by the same systems developed for the other dyes. Similarly the three vat dyes required a totally different separation system. Resources available for the project did not permit the development work necessary to separate and quantitate the vat dyes. Therefore, the final list of dyes studied included all those listed in Table 1 except the last 4 dyes. The selected dyes represent a broad range of chemical structures and application classes. Structures of the dyes that have been published are shown in Appendix B.

All dyes used in the study were commercial dyes obtained directly from dyestuff manufacturers. A variety of techniques were employed to obtain pure dye samples for preparation of standards.

#### A. Disperse Dye Purification

The disperse dyes were purified by placing a known weight of dye in a Soxhlet extraction thimble and extracting with a solvent for the dye until the extracting solvent was clear. The extract was then evaporated to dryness to recover the dye. The purified dye was subjected to exactly the same procedure a second time to obtain the samples used for standards. Toluene was the extraction solvent for all disperse dyes except Disperse Red 60. Benzene was the extraction solvent for Disperse Red 60. Dye purity was determined gravimetrically. The percent purity of the disperse dyes selected for study is shown in Table 2.

#### B. Acid, Direct and Reactive Dye Purification

Most of the acid, direct, and reactive dyes were purified by

Table 1  
Dyes Selected for Study

<u>C.I. Name</u>	<u>C. I. No.</u>	<u>Amount Used in *</u> <u>US 1982</u> <u>(Pounds)</u>
Acid Yellow 219	-	-
Acid Orange 156	-	1,962,000
Acid Red 266	17101	443,000
Acid Red 361	-	-
Acid Blue 25	62055	-
Acid Blue 40	62125	312,000
Acid Blue 277	-	-
Direct Yellow 106	40300	-
Direct Red 80	35780	332,000
Direct Blue 80	24315	244,000
Direct Black 80	31600	297,000
Disperse Yellow 23	26070	229,000
Disperse Yellow 42	10338	-
Disperse Yellow 54	47020	109,000
Disperse Red 60	60756	-
Disperse Red 73	11116	-
Disperse Red 135	-	-
Disperse Red 274	-	-
Disperse Blue 73	63265	-
Disperse Blue 77	-	-
Disperse Blue 79	-	6,642,000
Reactive Orange 4	18260	-
Reactive Red 2	18200	-
Reactive Blue 19	61200	-
Reactive Blue 21	-	-
Vat Yellow 2	67300/1	-
Vat Orange 7	71105	-
Vat Blue 6	69826/6	418,000

\*Where blanks are shown, the information is not available.

Table 2

## Pure Dye in Commercial Dye Samples

<u>C.I. Name</u>	<u>Purification Method</u>	<u>% Pure Dye</u>
Acid Yellow 219	Resin Adsorption	82.0
Acid Orange 156	Resin Adsorption	44.0
Acid Red 266	Resin Adsorption	46.2
Acid Red 361	Resin Adsorption	51.0
Acid Blue 25	Resin Adsorption	54.2
Acid Blue 40	Resin Adsorption	71.0
Acid Blue 277	Resin Adsorption	62.5
Direct Yellow 106	Resin Adsorption	32.4
Direct Red 80	Resin Adsorption	55.1
Direct Blue 80	Resin Adsorption	41.2
Direct Black 80	Resin Adsorption	49.9
Disperse Yellow 23	Toluene Extraction	38.2
Disperse Yellow 42	Toluene Extraction	65.1
Disperse Yellow 54	Toluene Extraction	23.9
Disperse Red 60	Benzene Extraction	30.8
Disperse Red 73	Toluene Extraction	43.9
Disperse Red 135	Toluene Extraction	32.3
Disperse Red 274	Toluene Extraction	36.9
Disperse Blue 73	Toluene Extraction	36.2
Disperse Blue 77	Toluene Extraction	58.0
Disperse Blue 79	Toluene Extraction	30.7
Reactive Orange 4	Resin Adsorption	83.1
Reactive Red 2	Resin Adsorption	67.9
Reactive Blue 19	Resin Adsorption	73.4



a resin adsorption procedure developed at Georgia Tech. A solution of the dye being purified was prepared in distilled water, filtered, and exposed to Amberlite XAD-2 resin beads which had been previously extracted with methanol and water. The beads were recovered by filtration and thoroughly washed with water. The adsorbed dye was then removed from the beads by methanol extraction in a Soxhlet unit. The dye extracted from the resin beads was then recovered by evaporation of the methanol. The dye purity was determined by comparison of the light absorption of standard solutions of the purified and commercial dye samples. Purities of the acid, direct and reactive dyes are given in Table 2.

For a number of the acid and direct dyes, the resin adsorption technique was compared with a precipitation purification method. In this method the dye is dissolved in dimethylformamide and precipitated by the addition of isopropanol. The dye is then recovered by filtration. In those cases studied, the resin adsorption technique appears to be equivalent to the precipitation method for dye purification.

## VI. Standard Solutions

Two bulk standard solutions were prepared, one containing disperse dyes and one containing acid, direct and reactive dyes. The disperse dye standard solution was prepared by carefully weighing a sufficient weight of each commercial disperse dye to give 1 gram of pure dye in the solution. The weighed dyes were transferred to a 1 liter volumetric flask and dissolved in 1% dimethylformamide and 99% benzene. This solution of 1 gram of each disperse dye per liter of solution was used to prepare 100, 20, 10, 5, 3, 1, and 0.5 part per million solutions of the disperse dyes by volumetric dilution.

Similar procedures were used to prepare a bulk solution of the reactive, direct and acid dyes except in this case the dyes were dissolved in 1% dimethylformamide-99% methanol. Analytical working standards similar to those described above for disperse dyes were prepared volumetrically.

## VII. Analytical Procedures

The samples recovered from the dye and control columns were subjected to several analytical procedures. They were each analyzed for the 24 dyes shown in Table 2 utilizing liquid chromatography and absorption spectrophotometry. They were also analyzed for priority pollutants as well as possible dye decomposition products using gas chromatography and mass spectrometry.

### A. Analysis for Dyes

Absorption spectrophotometry in the visible region of the spectrum can generally detect dyes in solution at less than 1 part-per-million. Since it was desirable in the current work to be able to detect dyes at the parts-per-billion level, a concentration step was necessary prior to separation and quantitation of the dyes. In previous work a concentration procedure based on adsorption of dye from wastewater on Amberlite XAD-2 resin followed by dye extraction with suitable solvents was utilized. This procedure works very well for acid and disperse dyes but it was not satisfactory for direct and reactive dyes, despite intensive efforts to find the correct conditions for adsorption and removal of the dyes. Either the larger sizes of the reactive and direct dyes were not compatible with the pore sizes in the resin or the resin-dye interaction was too strong for quantitative removal of the dye. This approach was abandoned in favor of concentration by solvent (water) evaporation. This approach can be taken because dyes are not volatile at low temperatures and are not lost when the solvent is evaporated.

One liter of each of the samples for analysis was evaporated to dryness in a Rotovap R110. The water was removed at temperatures less than 100°C under a mild laboratory vacuum. The solid residue was extracted repeatedly first with 99% benzene-1% dimethylformamide to remove the disperse dyes and then with 99% methanol-1% dimethylformamide to remove the acid, direct and reactive dyes. The extracts were diluted to 10 ml with the

appropriate solvents to give 100-fold increases in dye concentrations. Thus, a sample having 1 part-per-million dye in the liquid chromatography spectrophotometer detector would actually contain 10 parts-per-billion dye in the sample.

The recovery of dyes by this procedure was evaluated by preparing a 30 part-per-billion solution of the 24 dyes in 1 liter of Control Column effluent. This solution was subjected to the concentration procedure described above to evaluate the recovery process.

Dyes were separated by liquid chromatography and detected and quantitated by absorption spectrophotometry. Disperse dyes required one procedure for separation and analysis and the other dye classes (reactive, acid and direct) a second procedure. Thus, analysis of each sample required six chromatograms - three for disperse dyes with the detector set for red, yellow, and blue dyes and three for red, yellow and blue dyes of the other classes. The basic separation procedure has been described previously (5) but the procedure was improved and extended for the current work.

Disperse dyes were separated isocratically under the following conditions:

Column: 5N Partisil PAC  
Solvent: 80% Hexane, 20% Acetone  
Flow Rate: 1.5 ml/minute  
Sample Size: 20  $\mu$ l

For red dyes the detector was set at 510 nm, for blue dyes at 610 nm and for yellow dyes at 410 nm. Absorbance full scale was 0.02. Typical chromatograms are shown in Figures 3-5 for disperse yellow, red and blue dyes.

Separation of acid, direct and reactive dyes required use of gradient elution procedures using mixtures of methanol and distilled water. Separation conditions are shown below:

Column: C-18 reversed phase (Spherisorb ODS)  
Solvent: Methanol/Water with  
          tetrabutylammoniumphosphate (PIC A) added  
Gradient: 40/60 MEOH/H<sub>2</sub>O to 70/30 MEOH/H<sub>2</sub>O

30 minutes

exponent = 0.5

Flow Rate: 1.0 ml/minute

Sample Size: 20  $\mu$ l

Detector setups were the same as those given above for disperse dyes. Typical chromatograms are shown in Figures 6-8 for the red, yellow and blue acid, direct and reactive dyes.

As a check on the analytical procedure, the sample of Control Column Effluent spiked with 30 parts-per-billion of each of the dyes was concentrated and analyzed by exactly the same procedure as the column samples. Chromatograms of the Control Column Effluent with dyes (at 3 parts-per-million after the concentration step) is compared with a standard 3 parts-per-million sample in Figures 9-14. These comparisons were used to evaluate the dye recovery in the analytical system.

#### B. Analysis of Sludge Extracts

The mixed sludge used to fill the Dye Column was extracted and analyzed for dyes. It was originally planned to use sludge analysis to obtain the quantity of dye placed in the column but, despite repeated attempts, no way was found to remove dye quantitatively from sludge.

The acetonitrile extract of the sludge was analyzed and a large number of peaks were found in the chromatograms. Typical sludge extract chromatograms are shown in Figures 12-17. Peaks were present at positions expected for all the dyes selected for study. However, the number of peaks and the considerable peak overlap in the chromatograms make it impossible to conclude definitely that these peaks are from the dyes. Such a conclusion is not unreasonable in that the selected dyes were known to be in the influents to the plants generating the sludge from the inventory records of the textile dyeing operations discharging to the plants.

Table 3

Recovery of Dyes in the Concentration  
and Analysis System

<u>Dye</u>	<u>Recovery</u>
Acid Yellow 219	95%
Acid Orange 156	81%
Acid Red 266	61%
Acid Red 361	83%
Acid Blue 25	70%
Acid Blue 40	72%
Acid Blue 277	67%
Direct Yellow 106	9%
Direct Red 80	35%
Direct Blue 80	67%
Direct Black 80	- +
Disperse Yellow 23	95%
Disperse Yellow 42	81%
Disperse Yellow 54	83%
Disperse Red 60	85%
Disperse Red 73	83%
Disperse Red 135	77%
Disperse Red 274	67%
Disperse Blue 73	83%
Disperse Blue 77	- +
Disperse Blue 79	(80%)*
Reactive Orange 4	15%
Reactive Red 2	86%
Reactive Blue 19	- +

\* Estimated DB 79 not included in dye recovery sample

+ Could not be detected in recovered sample

Table 4

Detectability Limits of  
the 24 Dyes Selected for Study

<u>Dye</u>	<u>Detectability (ppb)</u>
Acid Yellow 219	2
Acid Orange 156	2
Acid Red 266	4
Acid Red 361	3
Acid Blue 25	5
Acid Blue 40	5
Acid Blue 277	4
Direct Yellow 106	10
Direct Red 80	10
Direct Blue 80	8
Direct Black 80	-
Disperse Yellow 23	5
Disperse Yellow 42	6
Disperse Yellow 54	2
Disperse Red 60	6
Disperse Red 73	1
Disperse Red 135	3
Disperse Red 274	3
Disperse Blue 73	4
Disperse Blue 77 *	-
Disperse Blue 79	2
Reactive Orange 4	30
Reactive Red 2	40
Reactive Blue 19 +	-

\* Could not be detected in any chromatograms

+ Could not be detected in dye recovery sample

Table 5

Aromatic Amine Standards  
Selected for GC-MS Analysis  
of Column Samples

1 - Aminonaphthalene  
2 - Methoxy-5-nitroaniline  
2,4 - Diaminotoluene  
3,3'- Dimethoxybenzidine  
2 - Amino-5-chlorobenzotrifluoride  
2 - Aminoanthraquinone  
2 - Methoxy-5-methylaniline  
4 - Aminophenol  
4-chloro-2-methylaniline  
p-Anisidine  
4-Nitroaniline  
o-Toluidine

## VIII. Results and Discussion

### A. Evaluation of Dye Recovery

Chromatograms of Control Column Effluent spiked with 30 parts-per-billion of each of the dyes in Table 1 and subjected to the 100 fold concentration procedure and a standard solution of 3 parts-per-million of each of the dyes are shown in Figures 9-14. These chromatograms were used to determine the per cent recovery of each of the dyes in the concentration procedure. It should be noted that this comparison includes all sources of losses including any errors in the analysis system.

The dye recovery data obtained are given in Table 3. In general the recovery of acid and disperse dyes was in the 70-80% range. For reasons that are not clear the direct dyes were very erratic in the percent recovery. Part of this is due to the fact that the direct dyes generally give much less intensive peaks in the chromatograms and therefore are subject to much higher error in determining concentrations.

Two dyes, Direct Blue 80 and Reactive Blue 19, could not be found in the recovered 30 ppb solution. This can be clearly seen by comparison of the chromatograms in Figure 10.

### B. Analysis of Column Effluents

Chromatograms of Dye Column and Control Column Effluents are shown in Figures 21-26. It is obvious in each case that the Dye Column chromatograms and the Control Column chromatogram are very similar and that there is no evidence for presence of dyes in any of the Dye Column Effluent chromatograms. Similar chromatograms of 0.5 ppm, 1 ppm or 3 ppm standard solutions of the 24 dyes selected from Table 2 are also shown in Figures 21-26 for comparison.

From the standard dye solution chromatograms and the per cent recovery data determined above it is possible to establish the lowest detection limit for most of the dyes. This was done by assuming that a peak whose height was twice the baseline noise level could be detected in the chromatograms. This number was



multiplied by the per cent recovery and divided by the concentration factor (100) to get the detectability limit. These values are given in Table 4 for each of the dyes. In the case of Disperse Blue 79, mislabelling of a dye sample by the manufacturer resulted in the omission of this dye in the recovery study. It seems reasonable to assume, based on the other disperse dyes, that a recovery of 80% would be reasonable for Disperse Blue 79. This value was used in calculating the detectability limit in Table 4 for Disperse Blue 79.

Thus, within the detectability limits shown in Table 4, no dyes were found in the effluents of the Control or the Dye Column.

Chromatograms of the Dye Column Interior are shown in Figures 27-32. It is apparent that the sample also has no dye concentrations greater than the detectability limit given in Table 4.

#### C. Analysis for Priority Pollutants

Samples of Control Column Effluent, Dye Column Effluent and Dye Column Interior were also analyzed for priority pollutants (see Appendix C) by standard methods (6). Standard Gas Chromatography-Mass Spectrometry techniques were used to analyze the concentrates for priority pollutants. This phase of the work was conducted under the direction of Dr. M.S. Black of the Georgia Tech Research Institute Environmental Health & Safety Division. Results of these analyses are shown in Tables 6-8.

#### D. Analysis for Dye Degradation Products

One possible mechanism for the degradation of azo dyes in the landfill environment is the reductive cleavage of the nitrogen-nitrogen double bond to produce aromatic amines. Samples of the aromatic amines shown in Table 5 were obtained as standards for gas chromatography-mass spectrometry analysis. These were chosen because they were expected degradation products of dyes in the study or because they were present on a list of 139 aromatic amines of interest to the U.S. Environmental

Table 6

Organic Compounds Found in  
Control Column Effluent Sample  
by GC-MS Analysis

<u>Compound</u>	<u>Sample 1 Concentration (ug/kg)</u>	<u>Sample 2 Concentration (ug/kg)</u>
3,3'-oxybispropanenitrile	0.42	0
3-methyl-2-heptanone	1.8	5.4
4-hydroxymethyl-2-methyl: 3,5-pyridinediol	0.66	1.8
1,12-tridecadiene	89	130

Differences in duplicates may be due to inhomogenous sample matrix. There appeared to be an oily layer on top of the water layer.

Table 7

Organic Compounds Found in  
Dye Column Effluent Sample  
by GC-MS Analysis

<u>Compound</u>	<u>Concentration (ug/kg)</u>
di-n-octyl-phthalate	12
Bis(2-ethylhexyl)phthalate	26
1-dodecanol	7.8
8-methyldecene	2.6
1,12-tridecadiene	480
1-Tridecene	5.6
Bicyclo (5.1.0)oct-3-ene	4.5

Table 8

Organic Compounds Found in  
Dye Column Interior Sample  
by GC-MS Analysis

<u>Compound</u>	<u>Concentration (ug/kg)</u>
Di-n-octyl-phthalate	12
Aniline	60
4-chloro-2-methylaniline	5.6
1,1'-biphenyl-2-amine	7.3
2,3-dihydro-2,3,3-trimethyl-1H-indole	4.2
1,3-dibutoxy-2-propanol	9.7
1,12-tridecadiene	210
Unidentified alcohol	140
6-nitro-3-picoline	4.4
3-bromodecane	4.3
Aromatic nitrogen containing compound (probable molecular weight of 261 base peak 77)	3.5

Protection Agency ("Class 1 Aromatic Amines"). The analysis for possible dye degradation products was conducted by the Environmental Health & Safety Division of the Georgia Tech Research Institute.

Gas chromatography-mass spectrometry (GC-MS) analysis of the Dye Column Effluent, the Control Column effluent and the Dye Column Interior are shown in Tables 6-8. The compounds in the Dye Column Effluent are typical plasticizers (commonly found in samples) or relatively large hydrocarbon molecules. Neither of these compound classes is likely to have originated from a dye degradation process.

The Dye Column Interior sample has some of the same compounds found in the Dye Column Effluent. The Interior sample also contains some compounds (aniline, 4-chloro-2-methylaniline, 1,1'-biphenyl-2-amine, 2-3 dihydro-2,3,3-trimethyl-1H-indole, 6-nitro-3-picoline) that may have been derived from dye degradation. Comparison of the structures of the dyes in this study with these possible degradation products does not suggest any of these dyes as the source of the compounds found. Acid Red 266 does have a chlorine bonded to an aromatic ring but it's difficult to see how 4-chloro-2-methylaniline could be derived from this dye. (It is possible that the 4-chloro-2-methylaniline may be derived from chlordimeform, a widely used pesticide.) Similarly Disperse Blue 80 contains a biphenyl group but it would not yield 1,1' biphenyl-2-amine on degradation. Disperse Yellow 54 contains a nitrogen in an aromatic structure but would not give 6-nitro-3-picoline on degradation. Structure of dyes in this study not disclosed in the literature were obtained from the dye manufacturers and these dyes also contained no structures that might be expected to give the compounds found. Thus, only aniline of the compounds in the GC-MS analysis may have come from degradation of the dyes in this study. There are a number of possible sources for the aniline found in the Dye Column Interior Sample. It could arise from reductive cleavage of the nitrogen-nitrogen double bond of azo dyes followed, if needed, by reductive stripping and removal of the substituent groups on the

derived aromatic amine. Aniline could also have been produced by breakdown of components other than dyes present in the sludge.

In an attempt to extend the search for dye degradation products, a series of standard amines were obtained and GC-MS spectra obtained for comparison with the column samples. The list of amines is shown in Table 5. None of these amines could be identified in the GC-MS study of the column samples. Several of those compounds did not separate well on the GC column used and would not have been found. However,

- 1 aminonaphthalene
- 2-methoxy-5-nitroaniline
- 2-amino-5-chlorobenzotrifluoride
- 2-methoxy-5-methylaniline
- 4-chloro-2-methylaniline
- o-toluidine

did yield good gas chromatograms and were definitely not detected in the column samples.

#### E. Adsorption of Dyes from Solution by Sludge

Since dyes were not found in the effluent from the Dye Column, were not found also in the Dye Column Interior and little evidence was discovered for dye degradation, the question that immediately presents itself is "What happens to the dyestuffs adsorbed on sludge that is placed in landfill?" Extensive experiments were conducted in an attempt to extract dyes quantitatively from sludge to complete a dye mass balance on the Dye Column. None of these experiments was successful.

A dye solution containing 0.50 ppm of each of the disperse, acid and direct dyes and 0.25 ppm of reactive dyes (commercial dye samples) was prepared to study the recovery of dyes from sludge. This solution was exposed in several experiments to sludge in a chromatography column. Sludge was obtained from the N.E. Clayton County sewage plant. This sludge contained about 0.9% dry solids. The sludge was allowed to settle, the supernatant decanted and the sludge washed with distilled H<sub>2</sub>O. This was repeated to remove any water soluble chemicals from the

sludge. The sludge was left in a closed container for thirty days to starve the bacteria. No bacterial count was made so it is possible that the sludge contained active bacteria. The sludge adsorption columns were prepared in 16 mm by 500 mm chromatography columns (Fisher and Porter). The column was fitted with a stopcock at the lower end preceded by an inch of packed glass wool to prevent sludge from seeping out of the column, but allowing the dye solution to pass through. Approximately 500 ml of sludge solution was allowed to settle and the top layer of H<sub>2</sub>O decanted. The column was then filled with sludge and the sludge was allowed to settle in the column. The stopcock was opened allowing excess water to drain off. This process was continued until the column was filled, leaving 1-inch at the top of the column for a glass wool plug. A Kelly infusion jar was attached to the column by a 2 inch piece of teflon tubing. Dye solution was poured into the infusion jar and passed slowly through the sludge packed column. The effluent was collected and analyzed for dye content. In some cases strands of glass fiber were included in the column to reduce sludge packing and to increase the rate of dye solution flow through the sludge. Thus, it was possible by knowing the concentration of dyes and volume of the influent to the sludge column and the dye concentration and volume of the effluent to determine the actual quantity of each dye adsorbed on the sludge.

Results of these experiments are shown in Table 9. It is apparent that at the concentrations investigated most dyes are quantitatively removed from water by sludge. Attempts to remove dyes from the sludge by solvent extraction using methanol, pyridine, dimethylformamide, benzene, acetone and various mixtures were relatively unsuccessful. Usually only 3 or 4 dyes could even be detected in the extract. The best acid dye extraction yielded 9.3% recovery of Acid Yellow 219, 18.7% recovery of Acid Red 266, 2.6% recovery of Acid Red 361 and 19.5% recovery of Acid Blue 277. The direct and reactive dyes exhibited lower per cent recoveries than the acid dyes. The best recovery that was achieved for the disperse dyes yielded 17.1% of

Disperse Yellow 23, 75% of Disperse Yellow 59, 80% of the Disperse Red 60 and 6.2% of Disperse Red 78. The other 5 disperse dyes were not detectable in the extract.

These results certainly suggest that the classes of dyes involved in this study are strongly adsorbed by waste treatment plant sludges and are very difficult to remove. This factor could explain the absence of detectable dye concentrations in the Dye Column Effluent and Interior samples.

#### IX. Conclusions

Analysis of effluents from a simulated landfill facility containing sludge from dye wastewater treatment plants showed no evidence of dyes. The detection limits were in the 1 to 10 parts per-billion range for most of the dyes in the study. Detectable concentrations of dyes were not found in similar analysis of water from the dye column interior.

Analysis of the effluents by GC-MS for priority pollutants did not yield any compounds that may reasonably have been generated by biological degradation of dyes. The column interior samples did contain several aromatic amines, but of the ones present, only aniline could possibly have been generated by degradation of some of the dyes in Table 1. A specific GC-MS search for several aromatic amines that may have been produced by degradation of dyes in the study was also unsuccessful.

It appears from studies on dyes in contact with waste treatment plant sludge that dyes are strongly adsorbed and tenaciously held by the sludge. This may explain the absence of dyes and dye degradation products in both the dye column effluent and dye column interior samples.



Table 9

## Dye Removed by Sludge

	<u>Disperse Dyes</u>							
	<u>Yellow 23</u>	<u>Yellow 42</u>	<u>Yellow 54</u>	<u>Red 60</u>	<u>Red 73</u>	<u>Red 135</u>	<u>Red 274</u>	<u>Blue 73</u> <u>Blue 79</u>
Run 1	100%	100%	85%	91%	100%	100%	100%	100%
Run 2	100%	100%	92%	94%	100%	100%	100%	100%
Run 3	94%	100%	68%	81%	100%	100%	100%	100%
Run 4	100%	100%	83%	93%	100%	100%	100%	100%

Reactive and Direct Dyes

	<u>D Yellow 106</u>	<u>D Red 80</u>	<u>D Blue 80</u>	<u>D Black 80</u>	<u>R Orange 4</u>	<u>R Red 2</u>	<u>R Blue 19</u>
Run 1	100%	100%	100%	100%	100%	100%	100%
Run 2	100%	100%	100%	100%	98%	100%	100%
Run 3	100%	100%	100%	100%	100%	100%	100%
Run 4	96%	100%	100%	100%	100%	89%	100%

Acid Dyes

	<u>Yellow 219</u>	<u>Orange 156</u>	<u>Red 266</u>	<u>Red 361</u>	<u>Blue 277</u>	<u>Blue 25</u>	<u>Blue 40</u>
Run 1	100%	79%	100%	100%	100%	100%	100%
Run 2	100%	100%	100%	100%	100%	100%	100%
Run 3	94%	100%	100%	100%	97%	100%	100%
Run 4	96%	100%	100%	100%	100%	100%	100%

## REFERENCES

1. Tincher, W. C. "Survey of the Coosa Basin for Organic Contaminants from Carpet Processing", Final Report Project E-27-630, Environmental Protection Division, Department of Natural Resources, State of Georgia, October, 1978.
2. Tincher, W. C. "Analysis for Acid Dyes in the Coosa River Basin", Final Project Report E-27-605, U. S. Operating Committee of the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry, Washington, D.C., February, 1986.
3. Dickson, D. W., "The Effectiveness of Biodegradation in the Removal of Acid Dyes and Toxicity From Carpet Dyeing Wastewater", Master's Thesis, Georgia Institute of Technology, March, 1986.
4. Shaul, G.M., U. S. Environmental Protection Agency, Cincinnati, Ohio, private communication.
5. Tincher, W. C. and Robertson, J. R., "Analysis for Dyes in Textile Dyeing Wastewater", Textile Chemist and Colorist, 14, 269 (1982).
6. Environmental Protection Agency Method 625.

APPENDIX A  
FIGURES 1-32

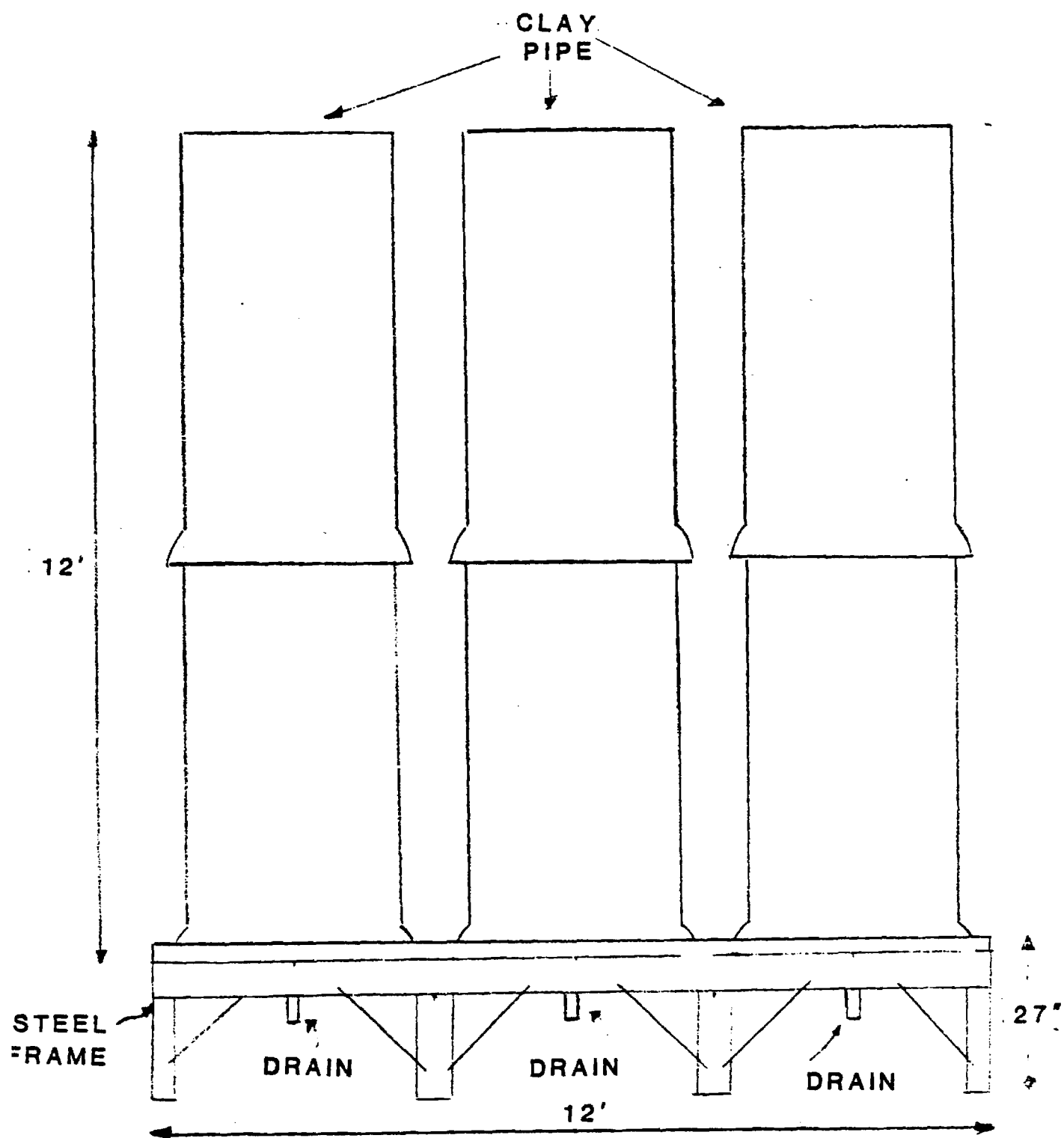


FIGURE 1 -- DESIGN OF SIMULATED LANDFILL FACILITY

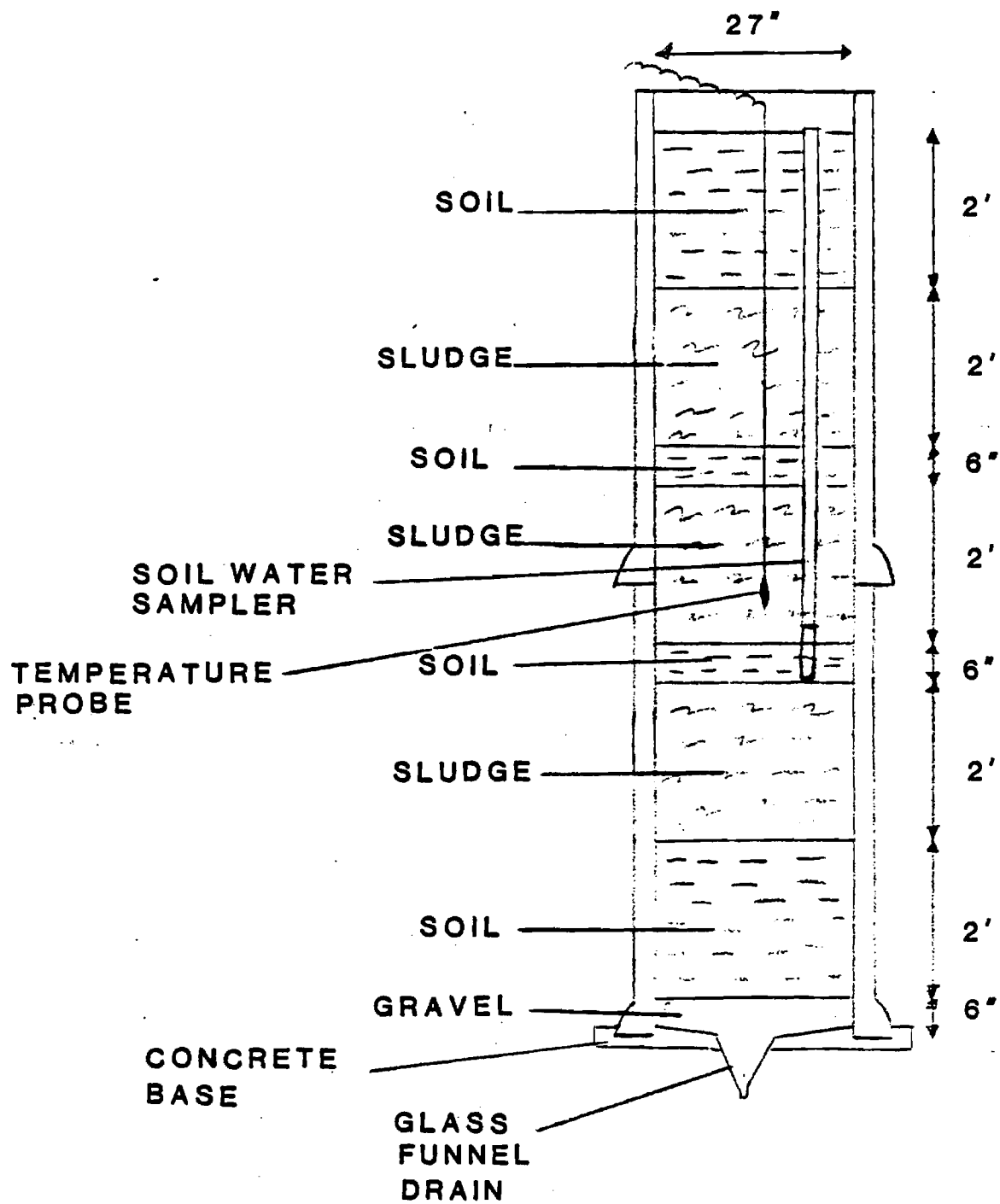


FIGURE 2 - - DETAILS OF COLUMN CONSTRUCTION AND FILLING

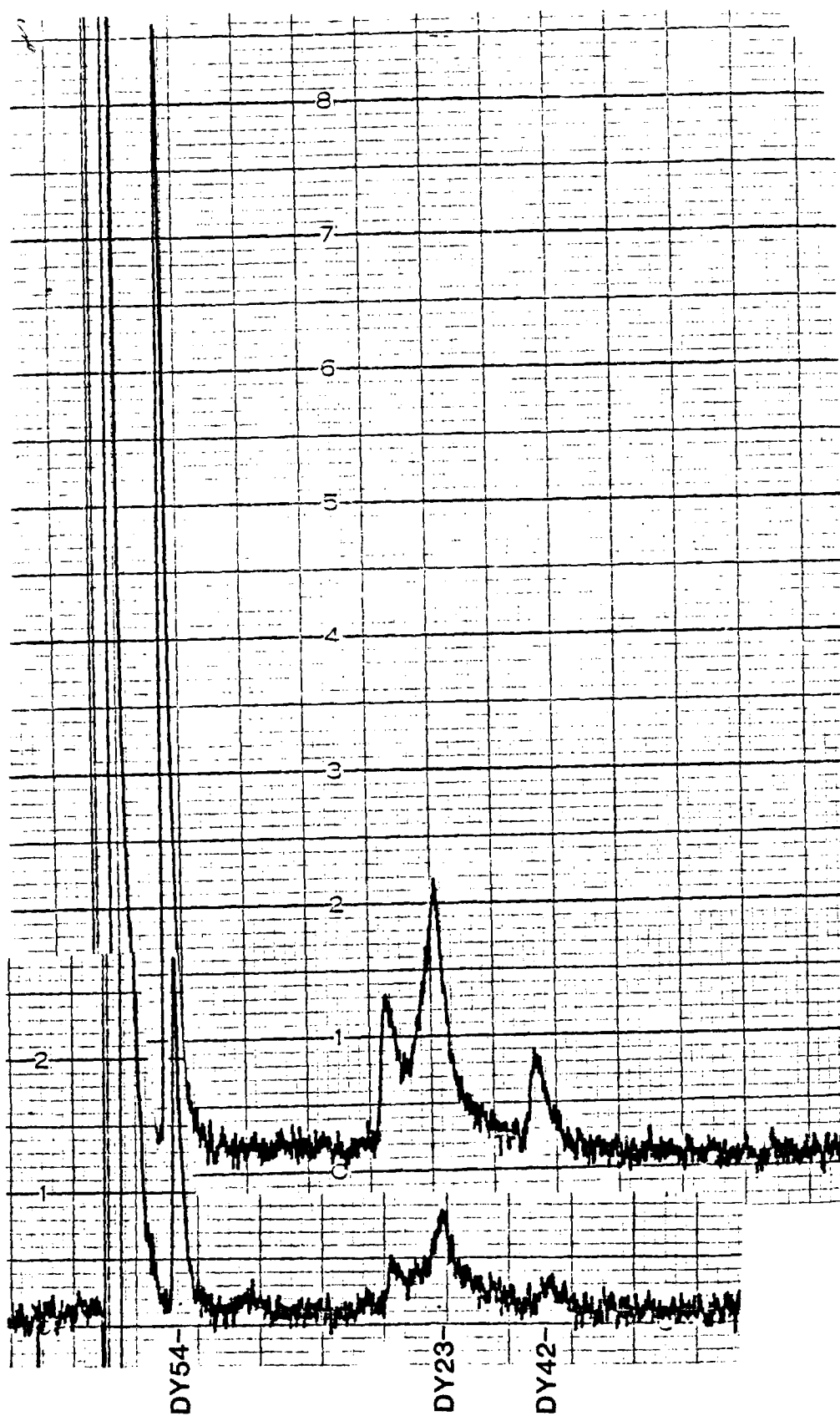


FIGURE 3 -- CHROMATOGRAMS OF DISPERSE YELLOW DYES  
(TOP: 3ppm, BOTTOM 1ppm IN BENZENE)

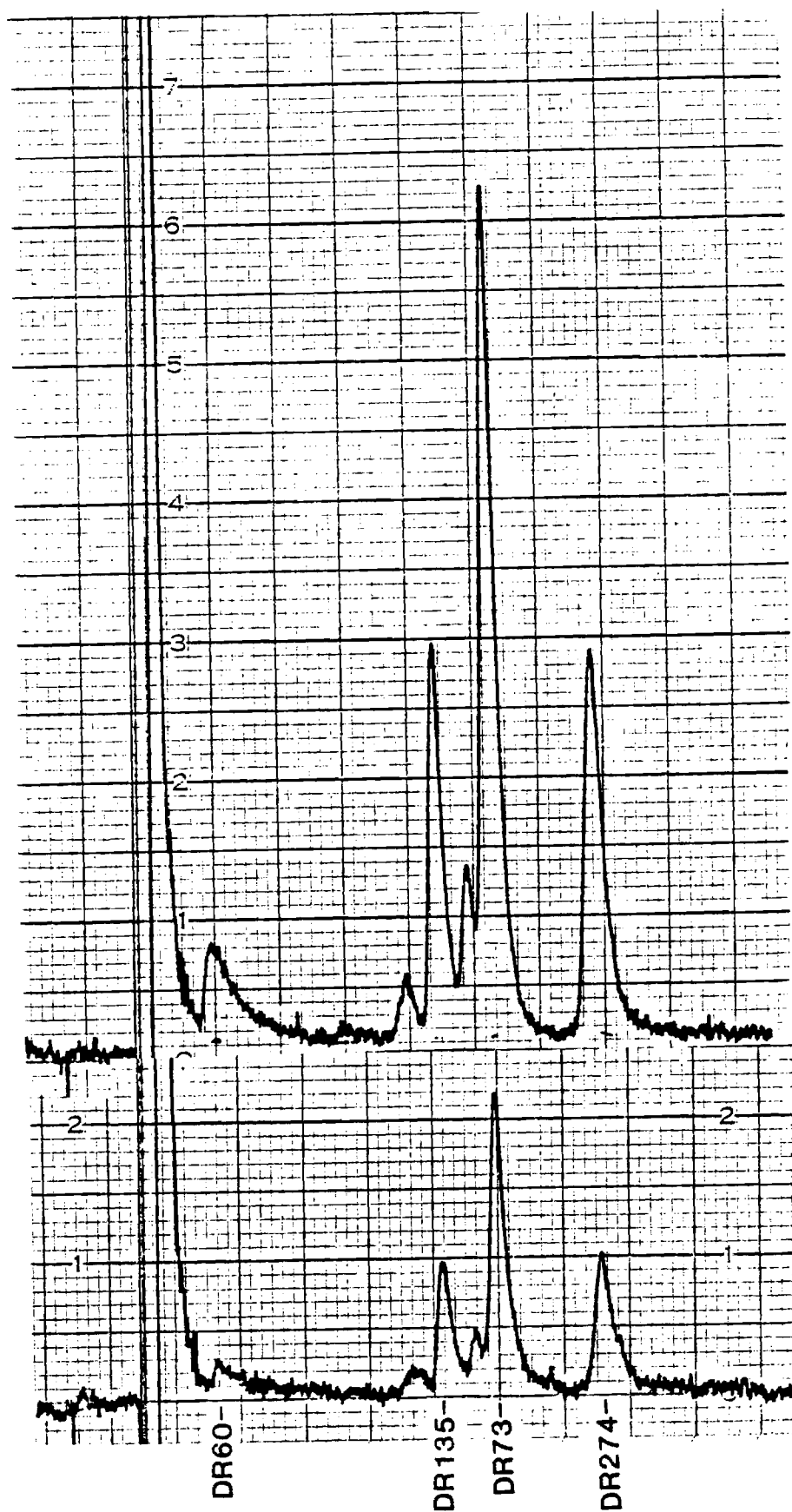


FIGURE 4 -- CHROMATOGRAMS OF DISPERSE RED DYES  
(TOP: 3ppm; BOTTOM 1ppm IN BENZENE)

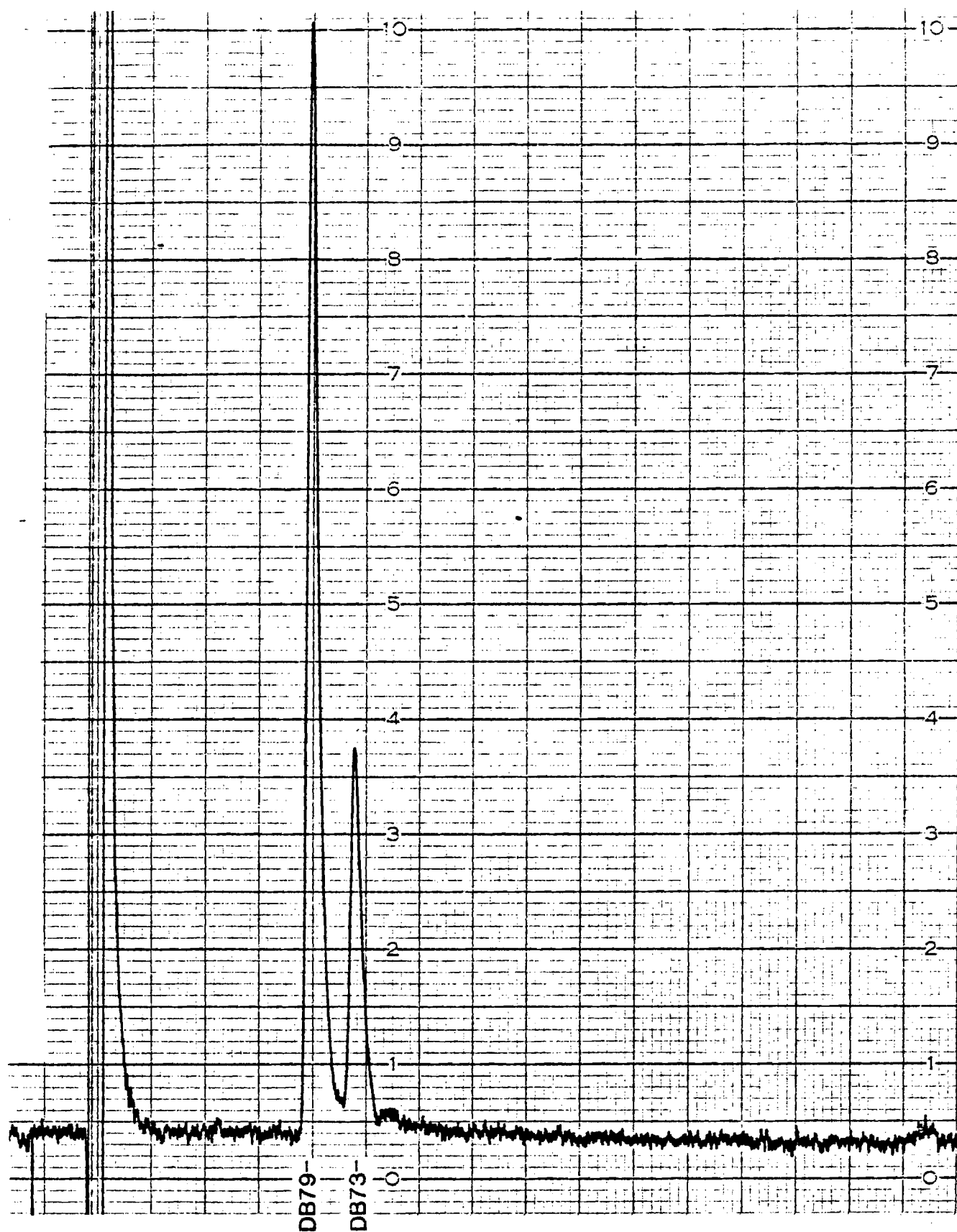


FIGURE 5 -- CHROMATOGRAM OF DISPERSE BLUE DYES (1ppm IN BENZENE)



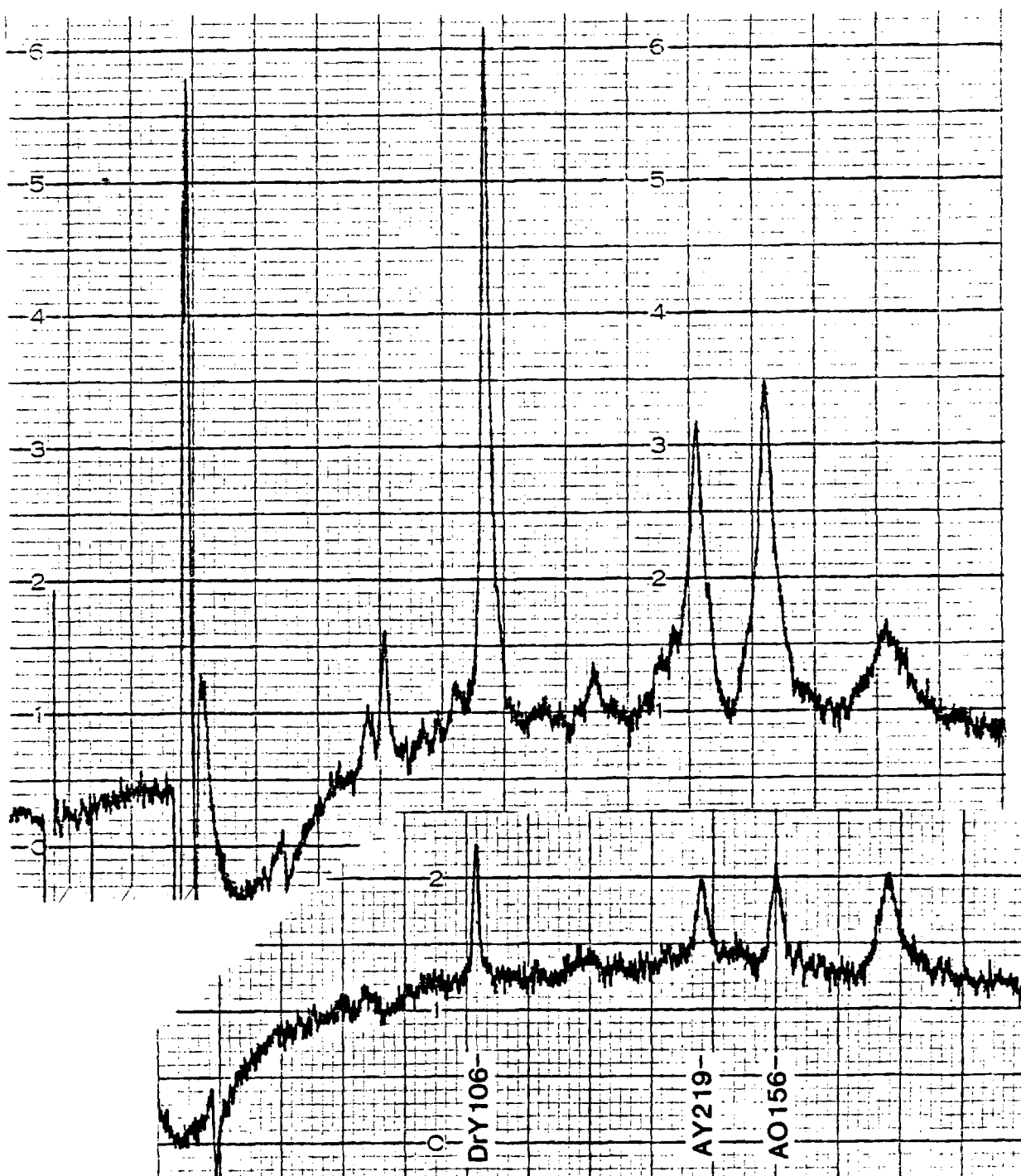


FIGURE 6 -- CHROMATOGRAMS OF DIRECT, REACTIVE AND ACID YELLOW DYES  
(TOP: 3ppm; BOTTOM 1ppm IN METHANOL)

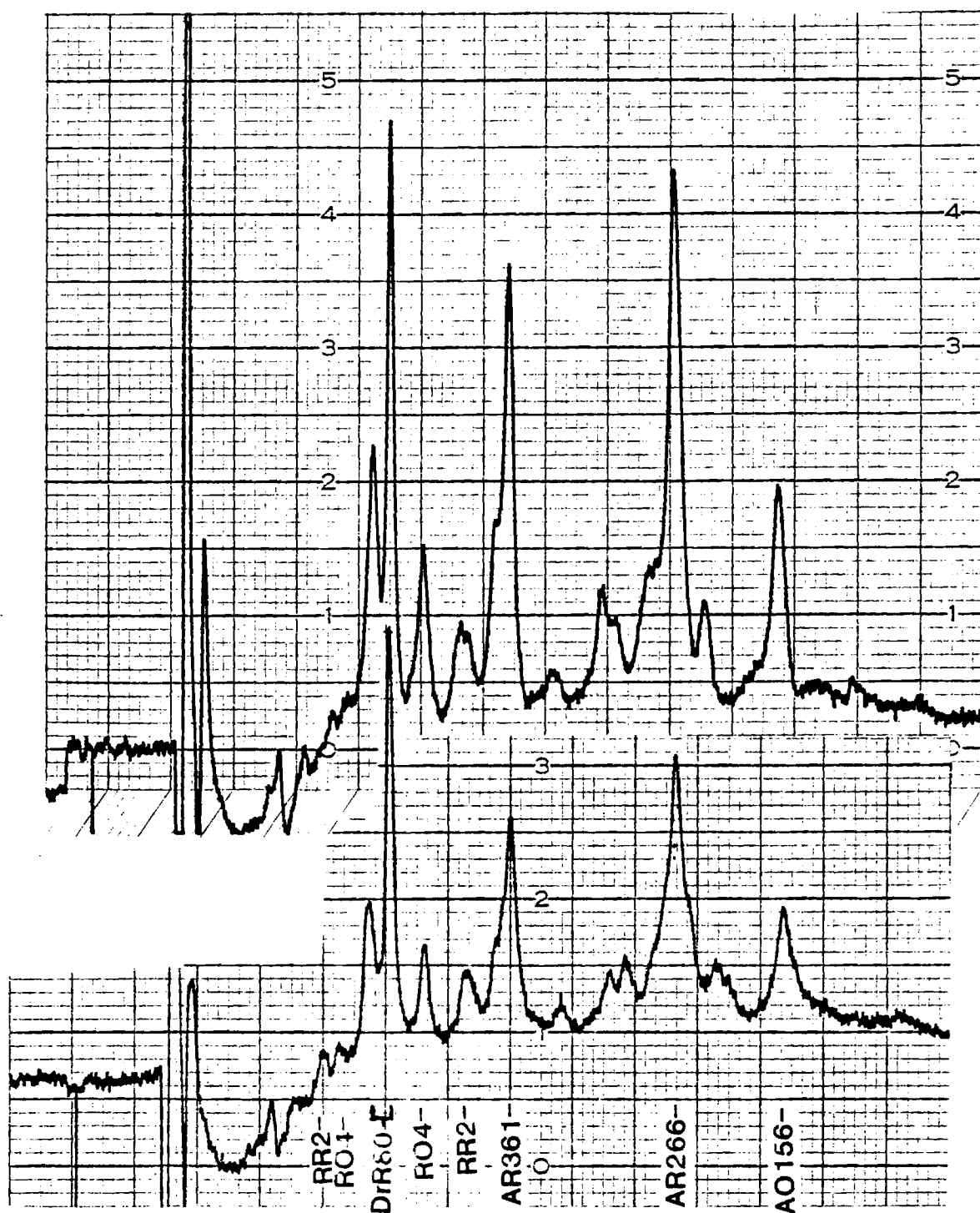


FIGURE 7 -- CHROMATOGRAMS OF DIRECT, REACTIVE AND ACID RED DYES  
(TOP: 5ppm, BOTTOM 3ppm IN METHANOL)

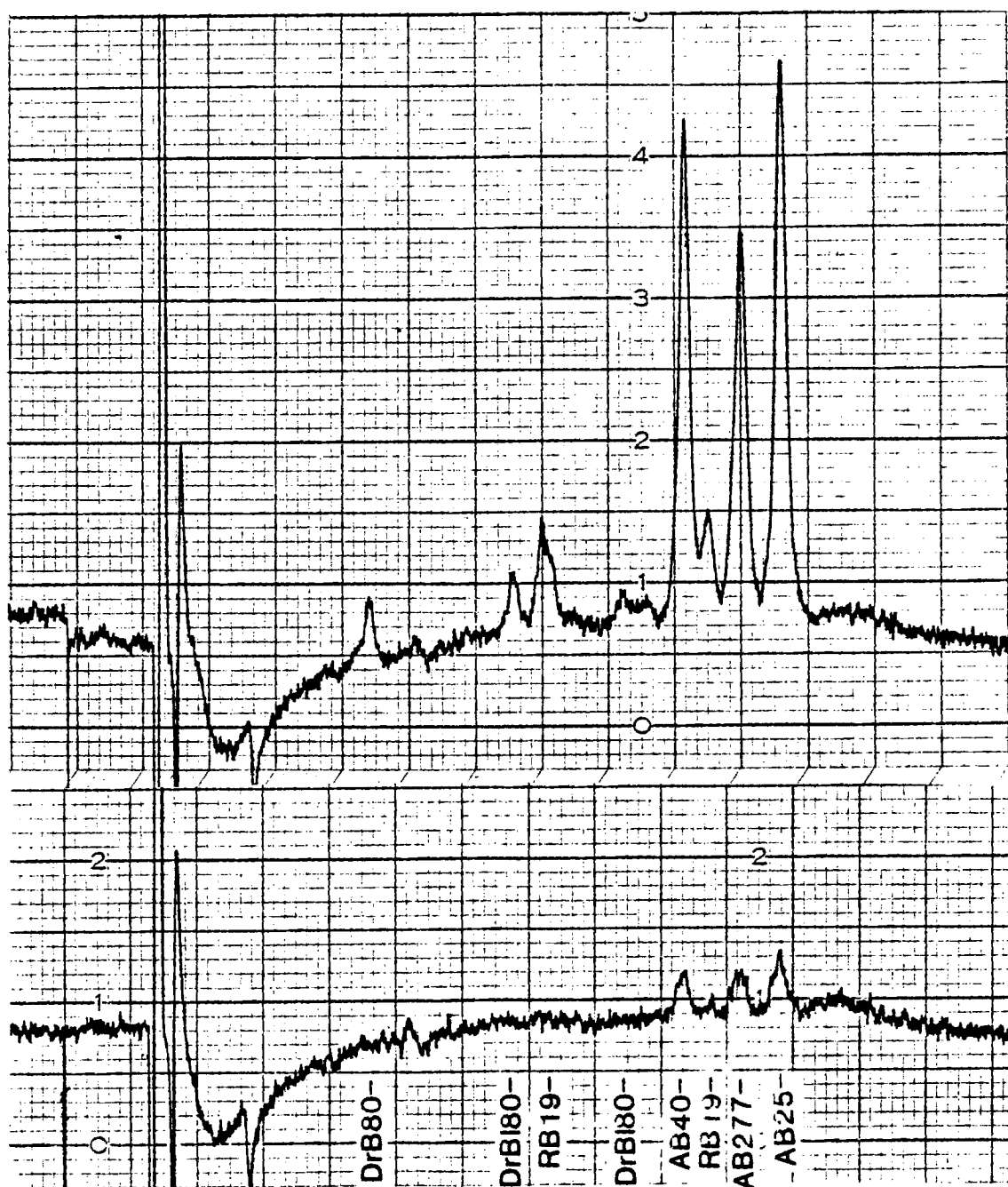


FIGURE 8 -- CHROMATOGRAMS OF DIRECT, REACTIVE AND ACID BLUE DYES  
(TOP: 3ppm, BOTTOM 0.5ppm IN METHANOL)

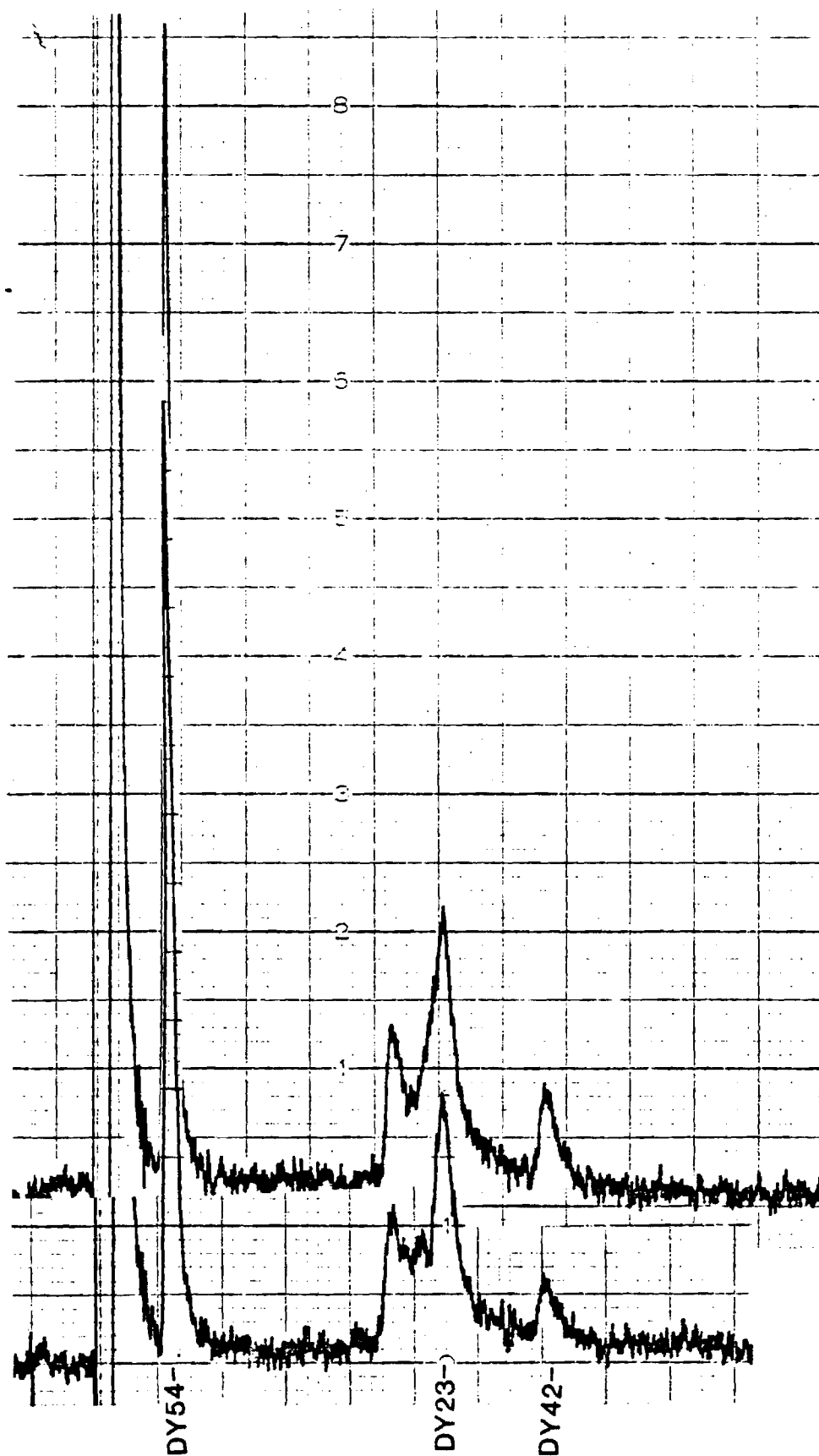


FIGURE 9 -- COMPARISON OF CHROMATOGRAMS OF 3ppm STANDARD (TOP) AND SPIKED 30ppb CONTROL COLUMN EFFLUENT X100 (BOTTOM) OF DISPERSE YELLOW DYES



FIGURE 10 -- COMPARISON OF CHROMATOGRAMS OF 3ppm STANDARD (TOP) AND 30PPB SPIKED CONTROL COLUMN EFFLUENT (BOTTOM) OF DISPERSE RED DYES

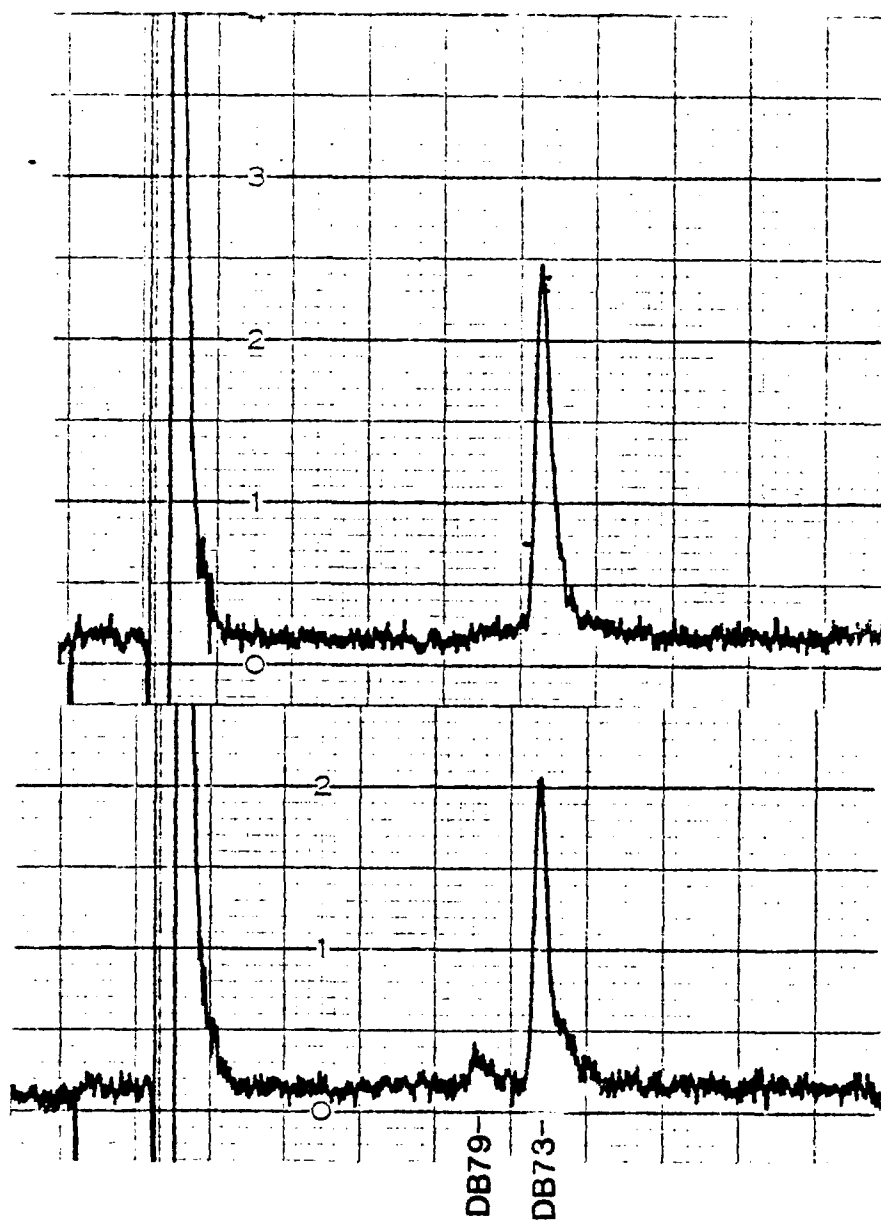


FIGURE 11 -- COMPARISON OF CHROMATOGRAMS OF 3ppm STANDARD (TOP) WITH 30ppb SPIKED CONTROL COLUMN EFFLUENT X100 (BOTTOM) OF DISPERSE BLUE DYES

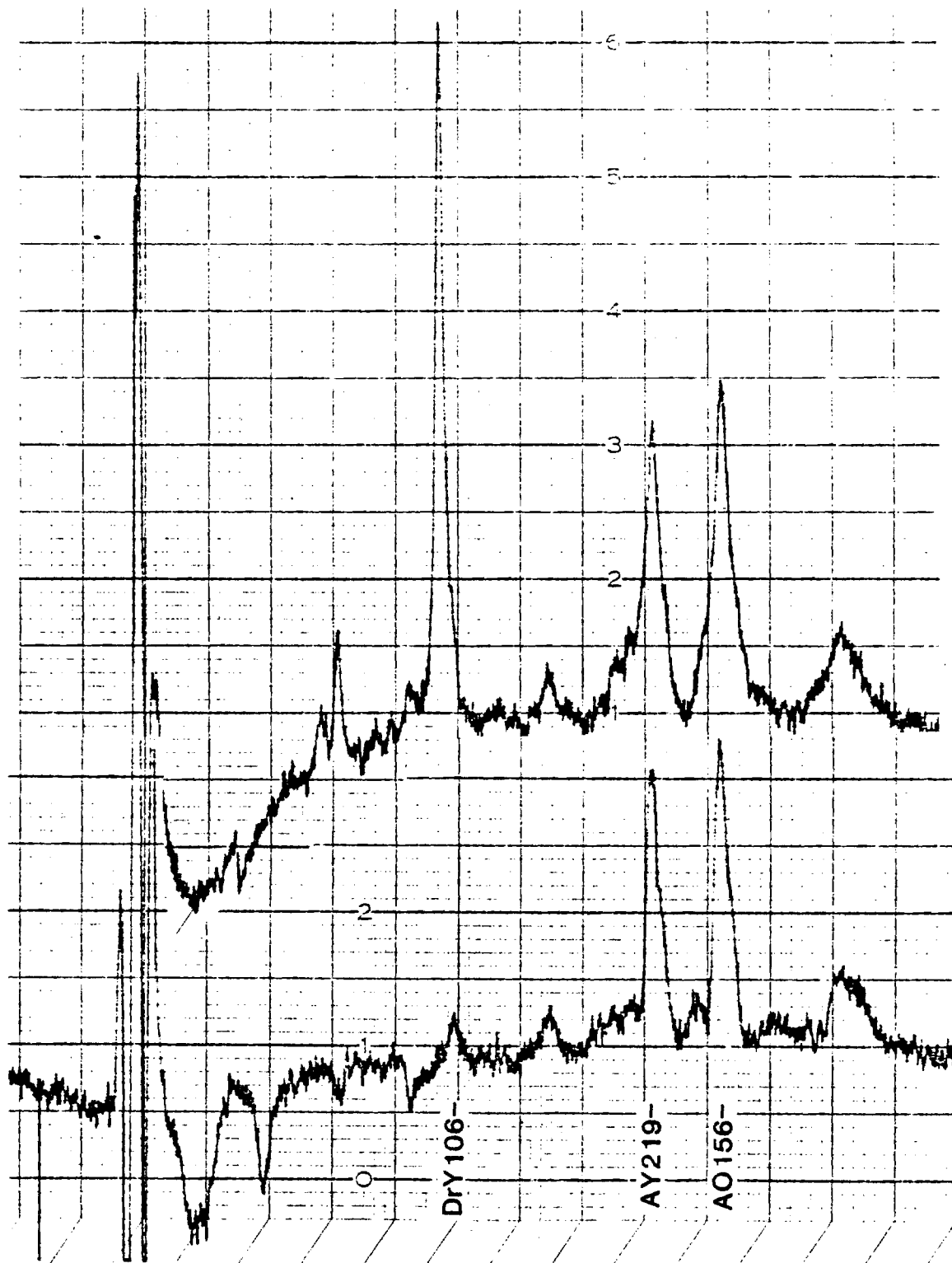


FIGURE 12 -- COMPARISON OF CHROMATOGRAMS OF 3ppm STANDARD (TOP) WITH 30ppb SPIKED CONTROL COLUMN EFFLUENT X100 (BOTTOM)-DIRECT, ACID AND REACTIVE YELLOW DYES

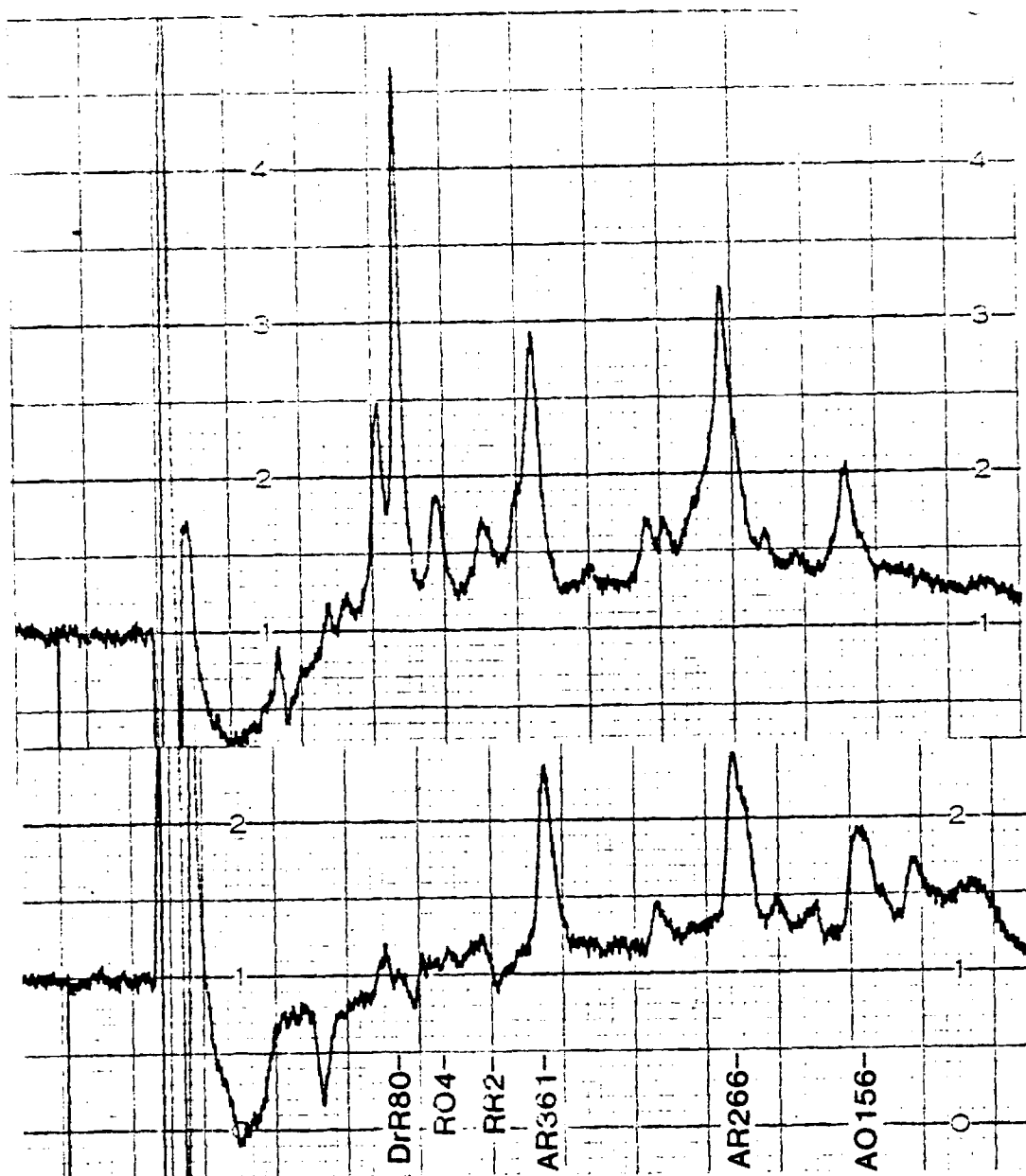


FIGURE 13 -- COMPARISON OF CHROMATOGRAMS OF 3ppm STANDARD (TOP) WITH 30ppb SPIKED CONTROL COLUMN EFFLUENT (X100) (BOTTOM) DIRECT, ACID, AND REACTIVE RED DYES



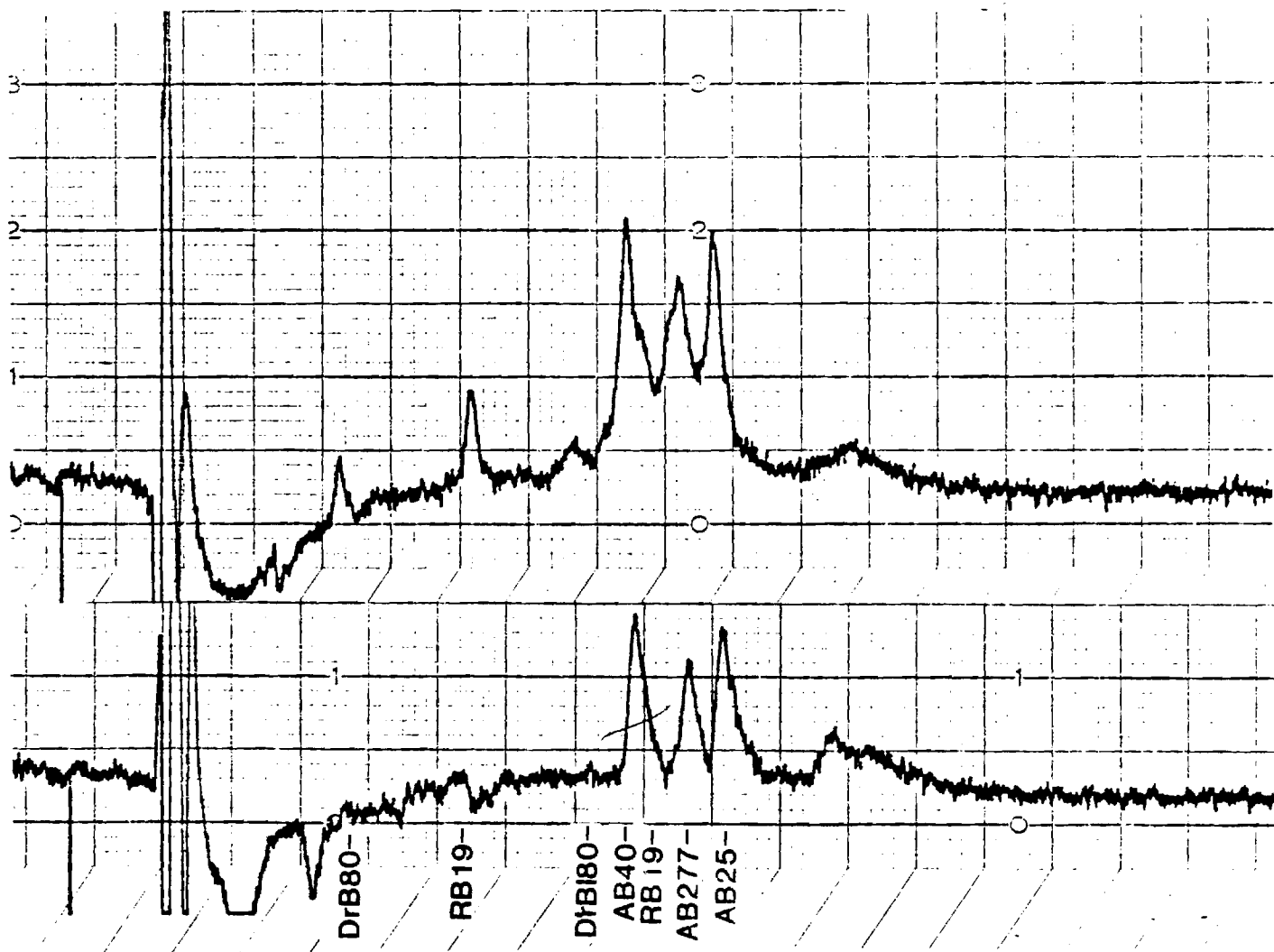


FIGURE 14 -- COMPARISON OF CHROMATOGRAMS OF 3ppm STANDARD (TOP) WITH 30ppm SPIKED CONTROL COLUMN EFFLUENT (X100) (BOTTOM) OF DIRECT, ACID, AND REACTIVE BLUE DYES

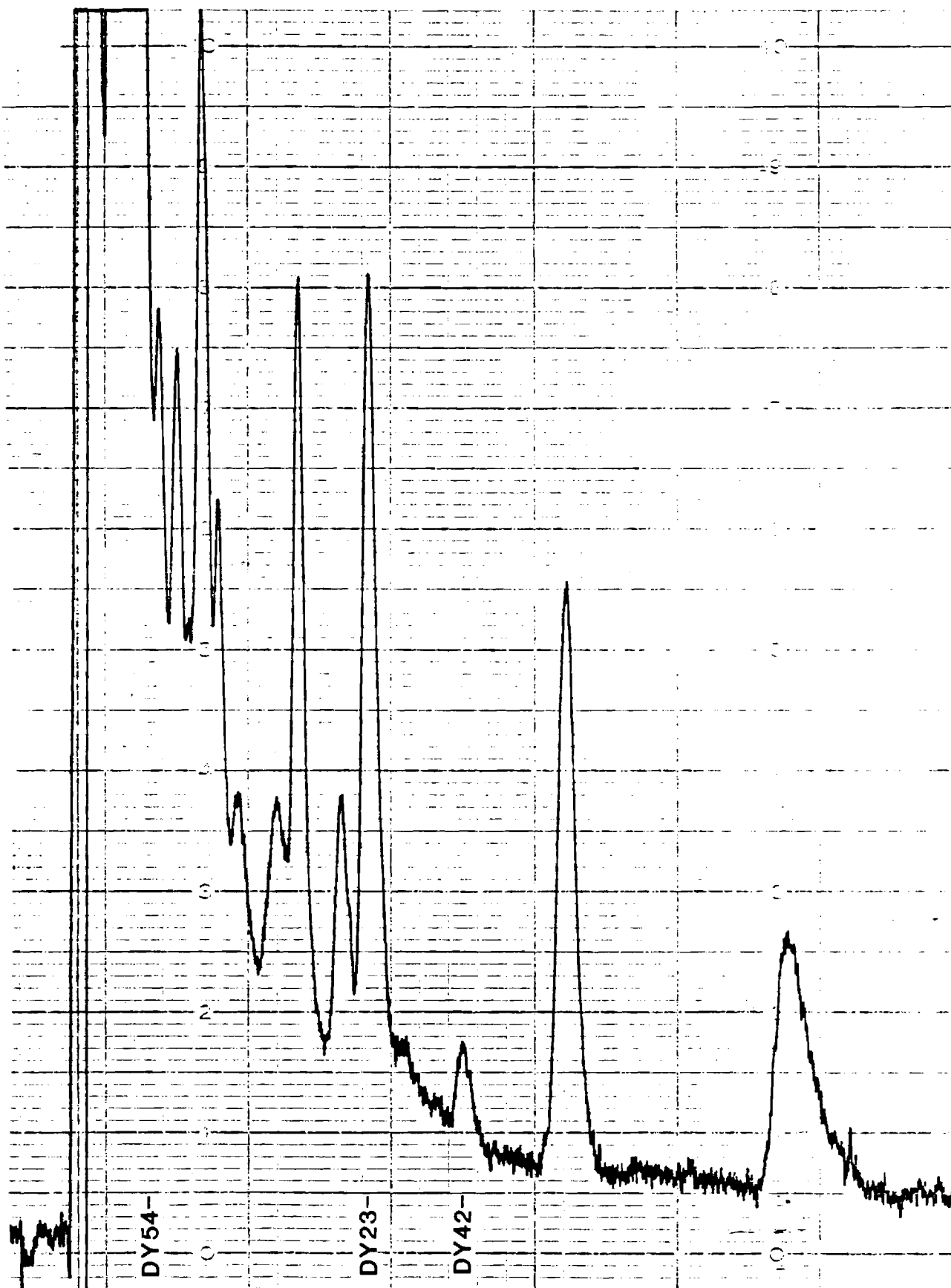


FIGURE 15 -- CHROMATOGRAM OF SLUDGE EXTRACT-DISPERSE YELLOW DYES

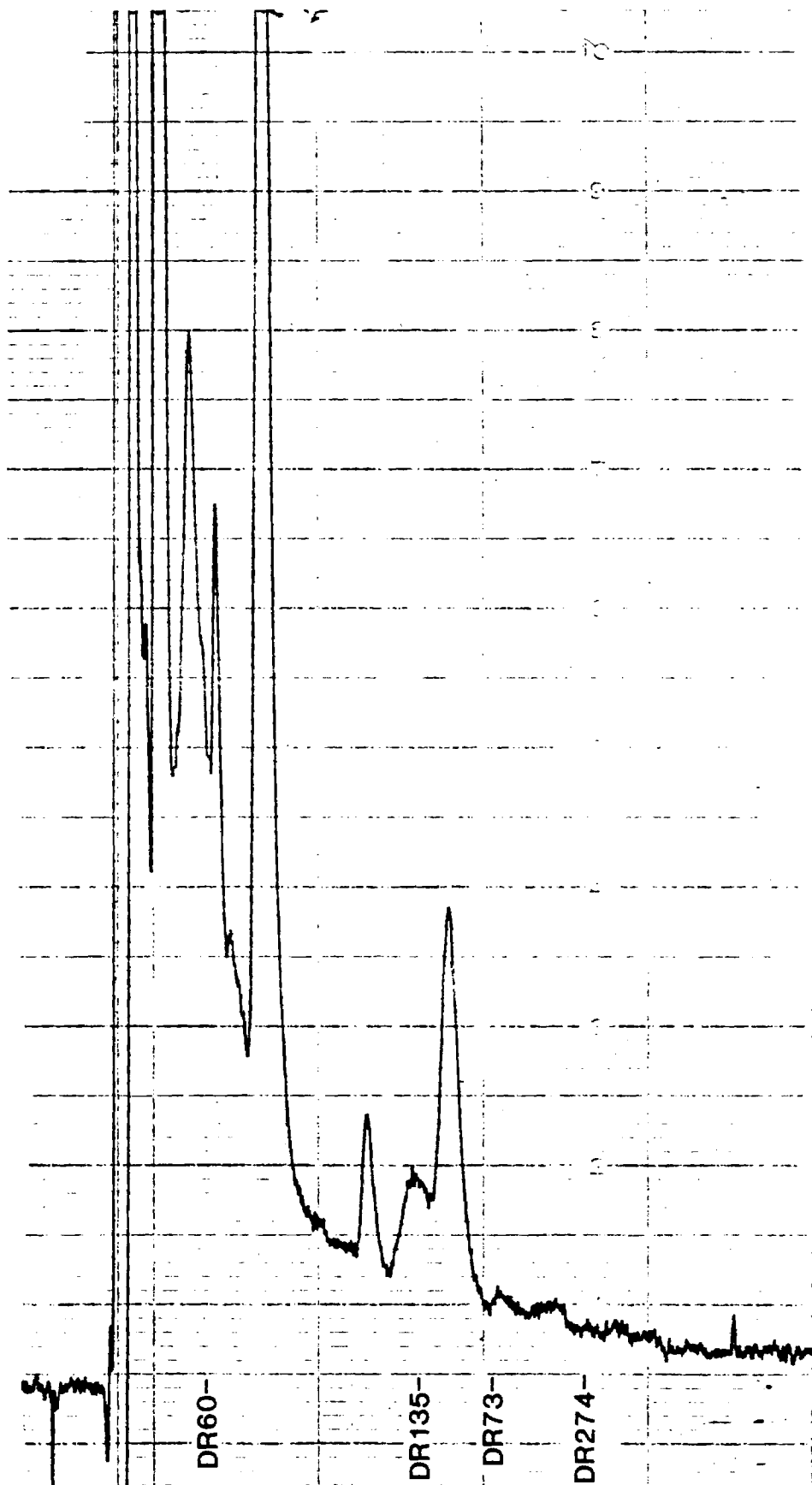


FIGURE 16 -- CHROMATOGRAM OF SLUDGE EXTRACT-DISPERSE RED DYES

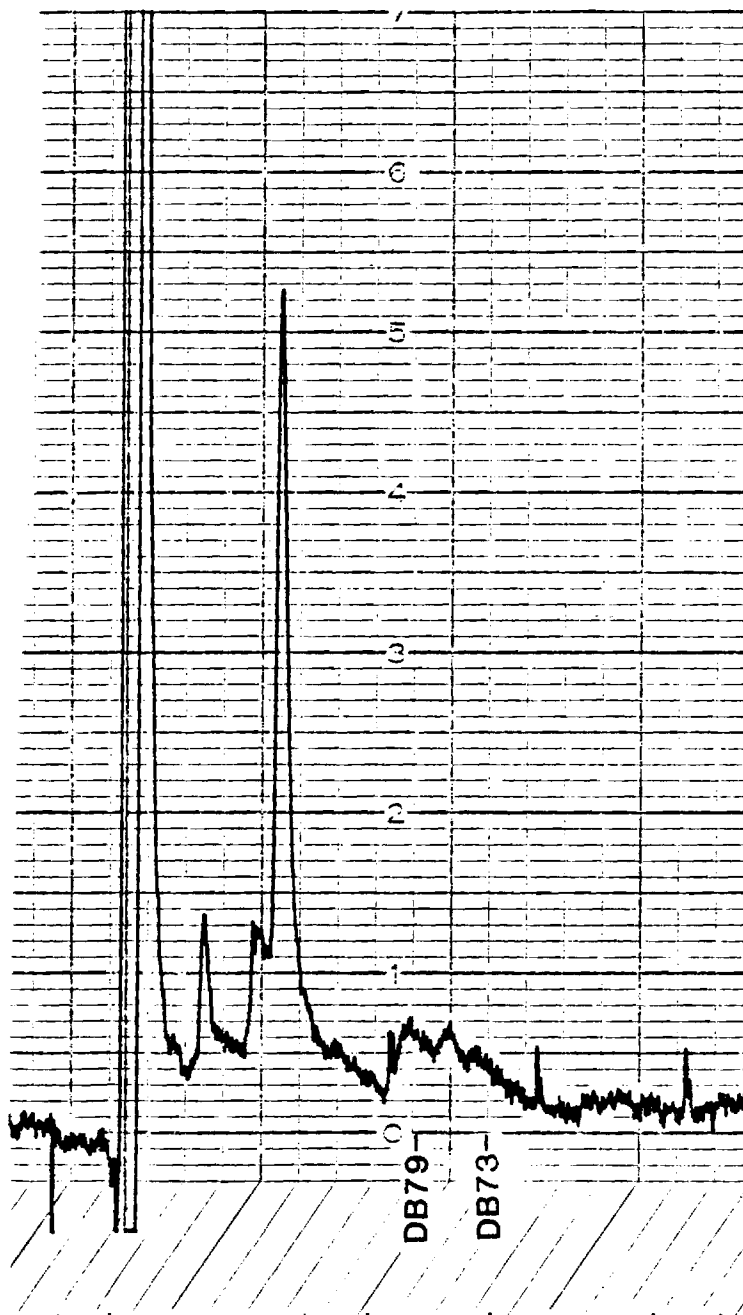


FIGURE 17 -- CHROMATOGRAM OF SLUDGE EXTRACT DISPERSE -  
DISPERSE BLUE DYES

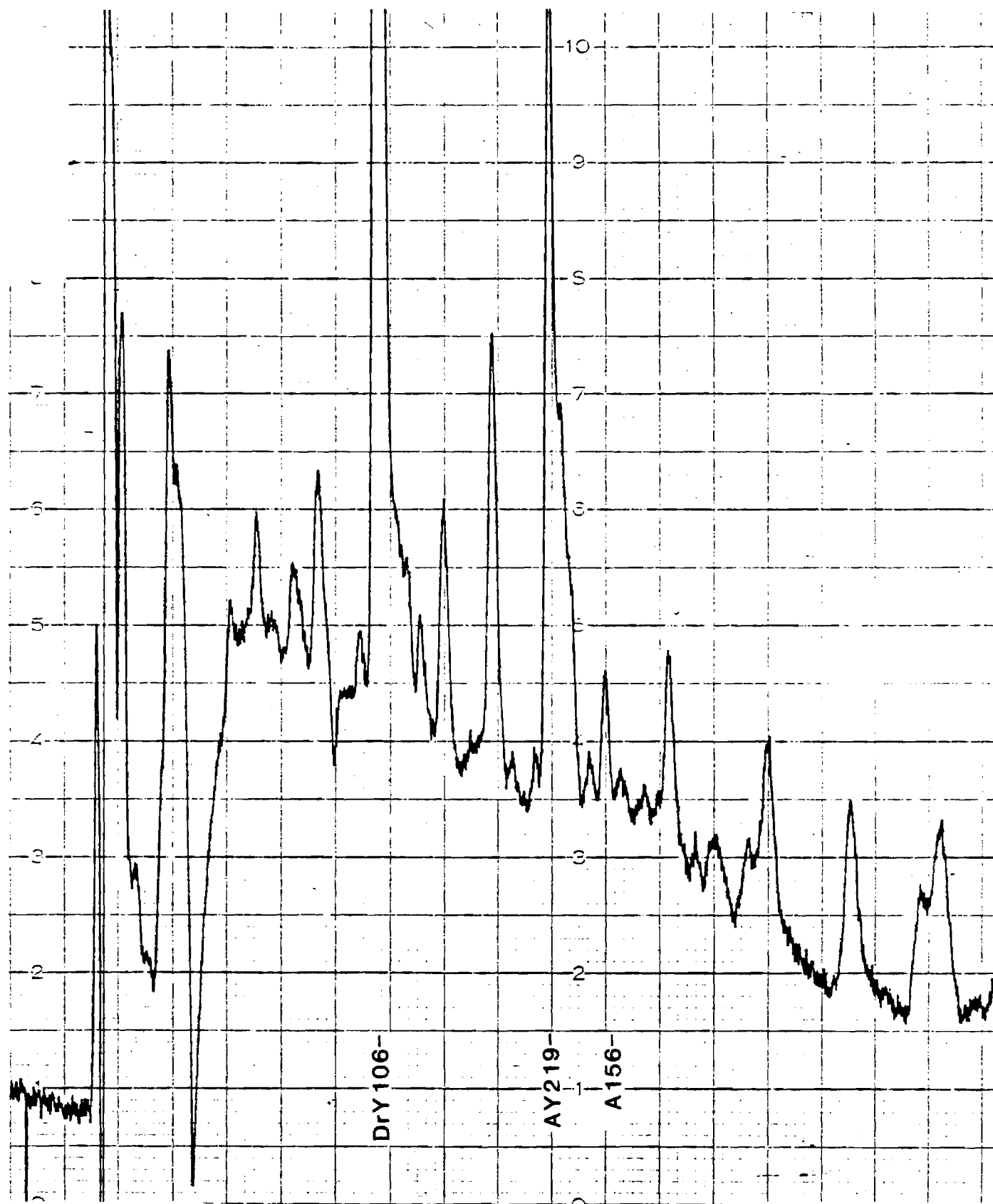


FIGURE 18 -- CHROMATOGRAM OF SLUDGE EXTRACT - DIRECT, ACID AND REACTIVE YELLOW DYES

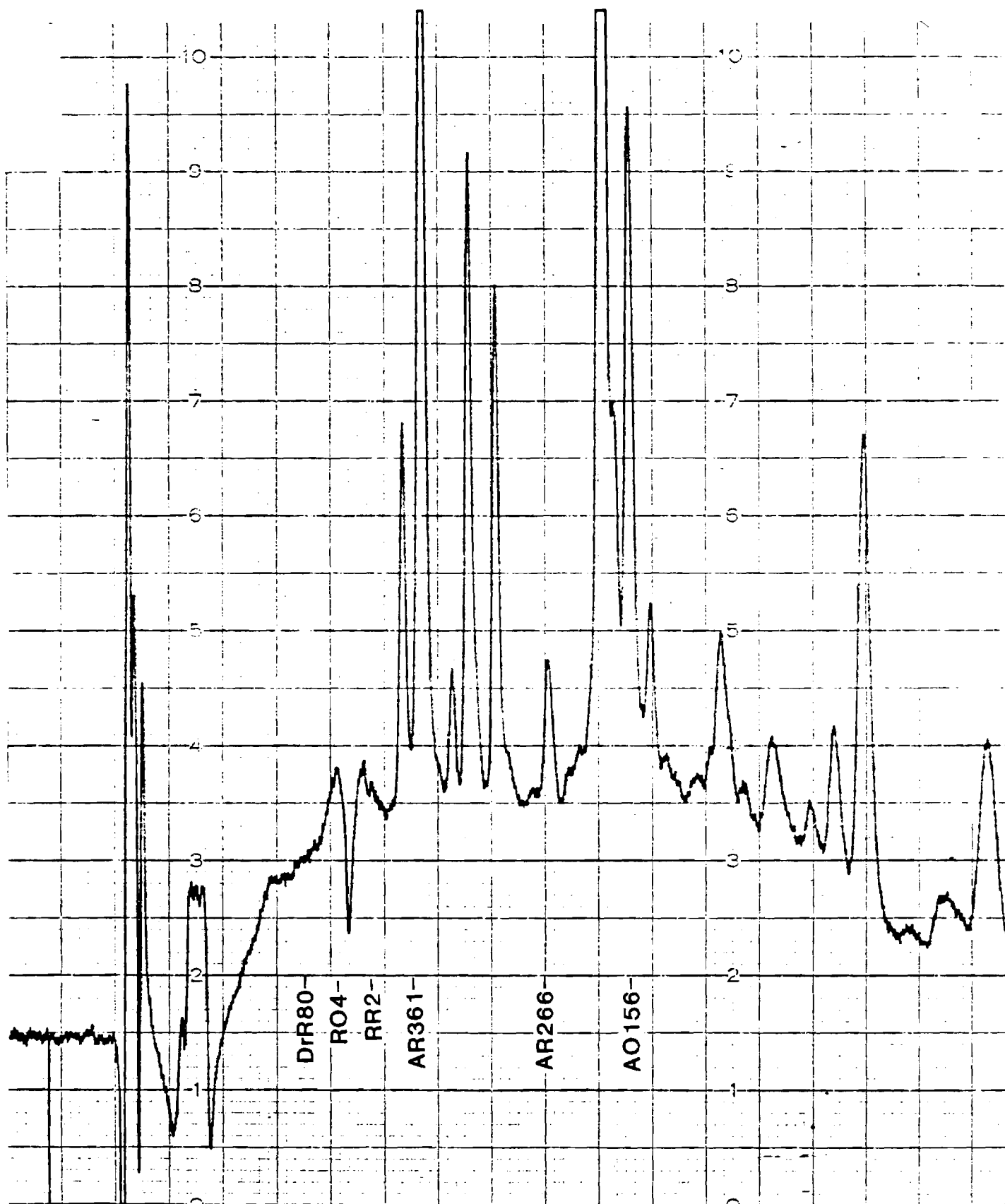


FIGURE 19 -- CHROMATOGRAM OF SLUDGE EXTRACT - DIRECT, ACID AND REACTIVE RED DYES

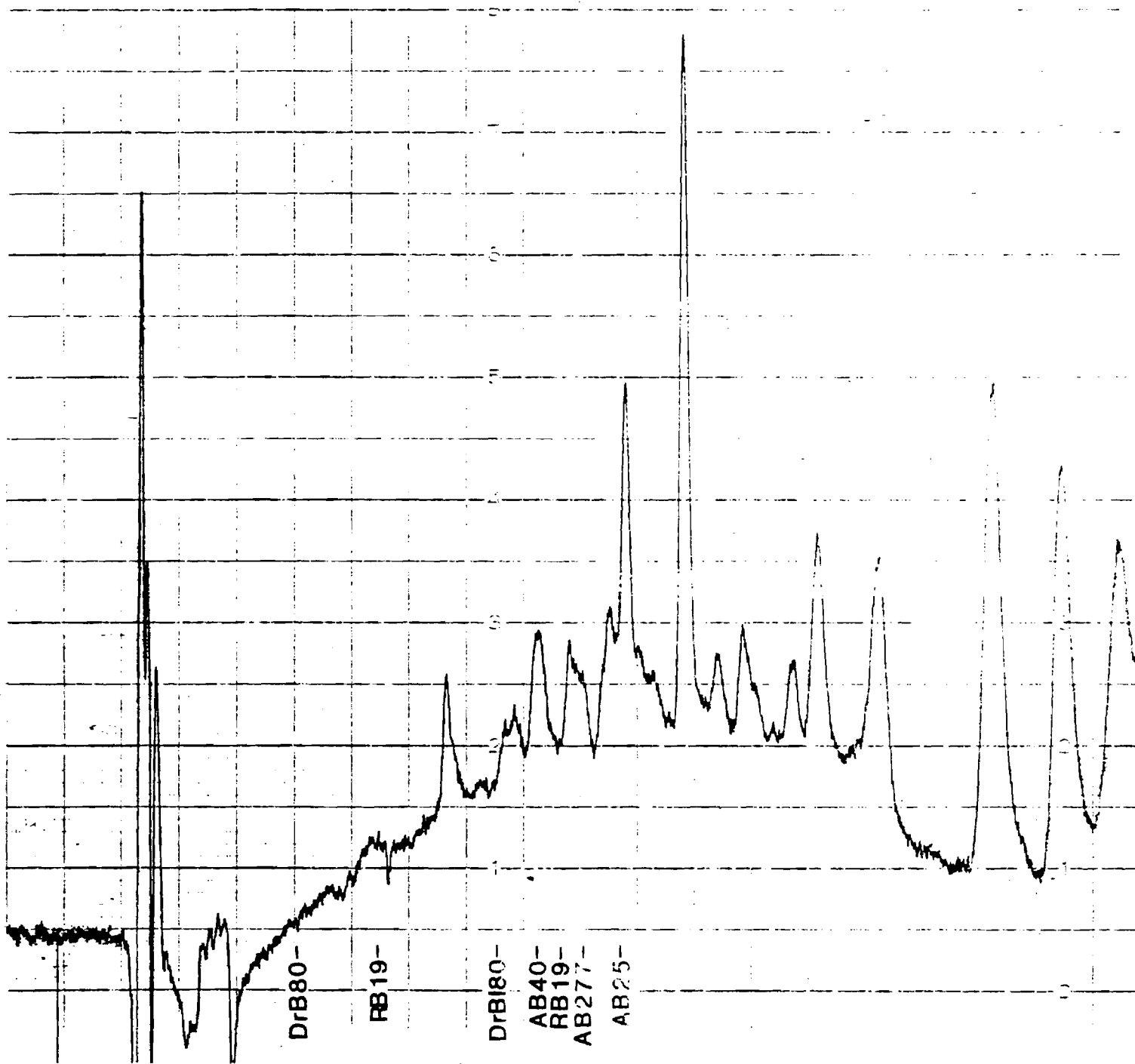


FIGURE 20 -- CHROMATOGRAM OF SLUDGE EXTRACT - DIRECT, ACID AND REACTIVE BLUE DYES

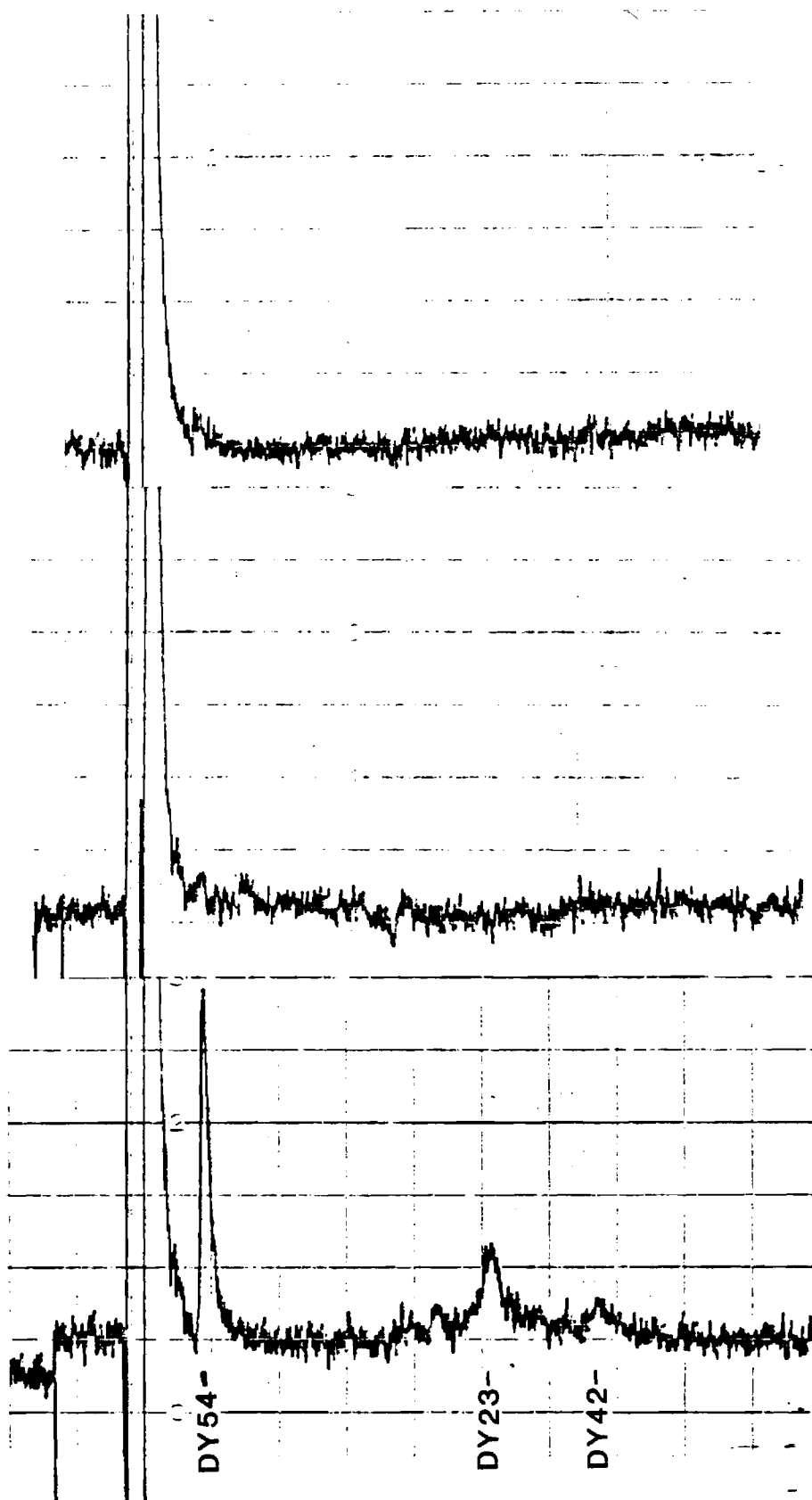


FIGURE 21 -- CHROMATOGRAMS OF COLUMN EFFLUENTS - CONTROL COLUMN (TOP),  
DYE COLUMN (MIDDLE), 1ppm STANDARD DISPERSE YELLOW DYES



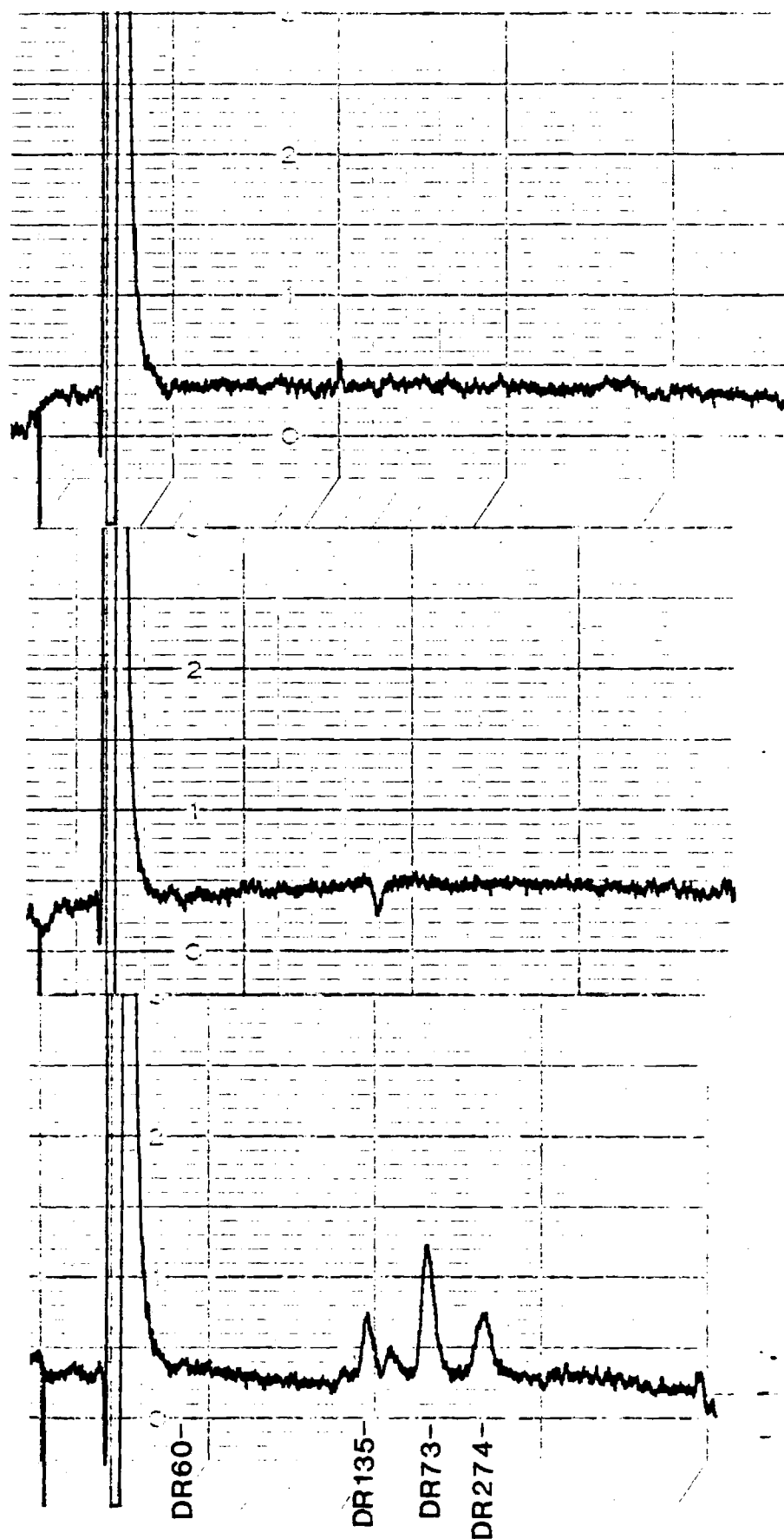


FIGURE 22 -- CHROMATOGRAMS OF COLUMN EFFLUENTS: CONTROL COLUMN (TOP) DYE COLUMN (MIDDLE) 0.5ppm STANDARD DISPERSE RED DYES



FIGURE 23 -- CHROMATOGRAMS OF COLUMN EFFLUENTS - CONTROL COLUMN (TOP), DYE COLUMN (MIDDLE) 1.0ppm STANDARD DISPERSE BLUE DYE SOLUTION (BOTTOM)

NOTE: Sharp peaks in column effluents due to sticking value in HPLC pump during these runs.

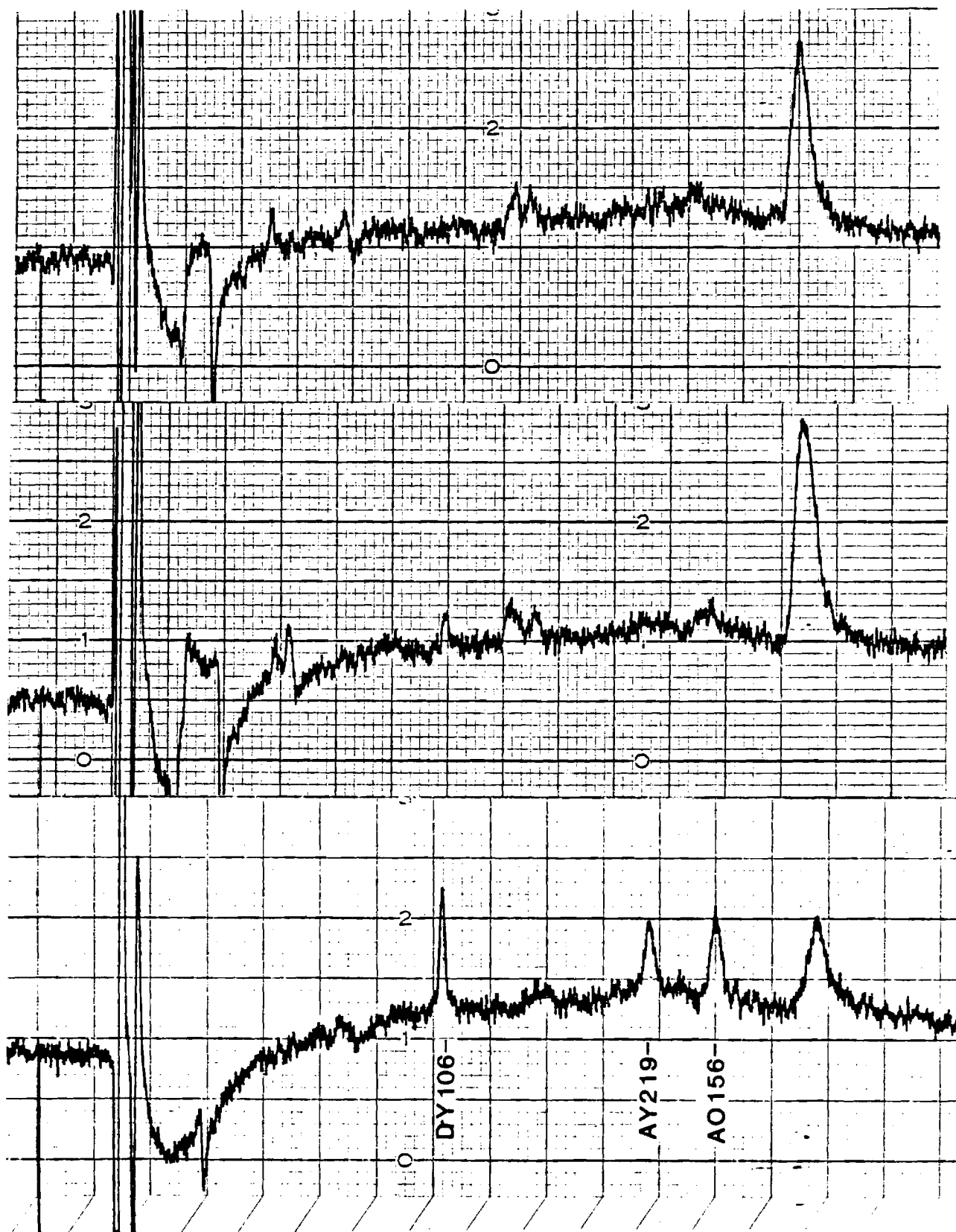


FIGURE 24 -- CHROMATOGRAMS OF COLUMN EFFLUENTS - CONTROL COLUMN (TOP), DYE COLUMN (MIDDLE), 0.5ppm STANDARD SOLUTION DIRECT, ACID, AND REACTIVE DYES (BOTTOM)



FIGURE 25 -- CHROMATOGRAMS OF COLUMN EFFLUENTS CONTROL COLUMN (TOP), DYE COLUMN (MIDDLE), AND 3ppm STANDARD DIRECT, ACID AND REACTIVE RED DYES

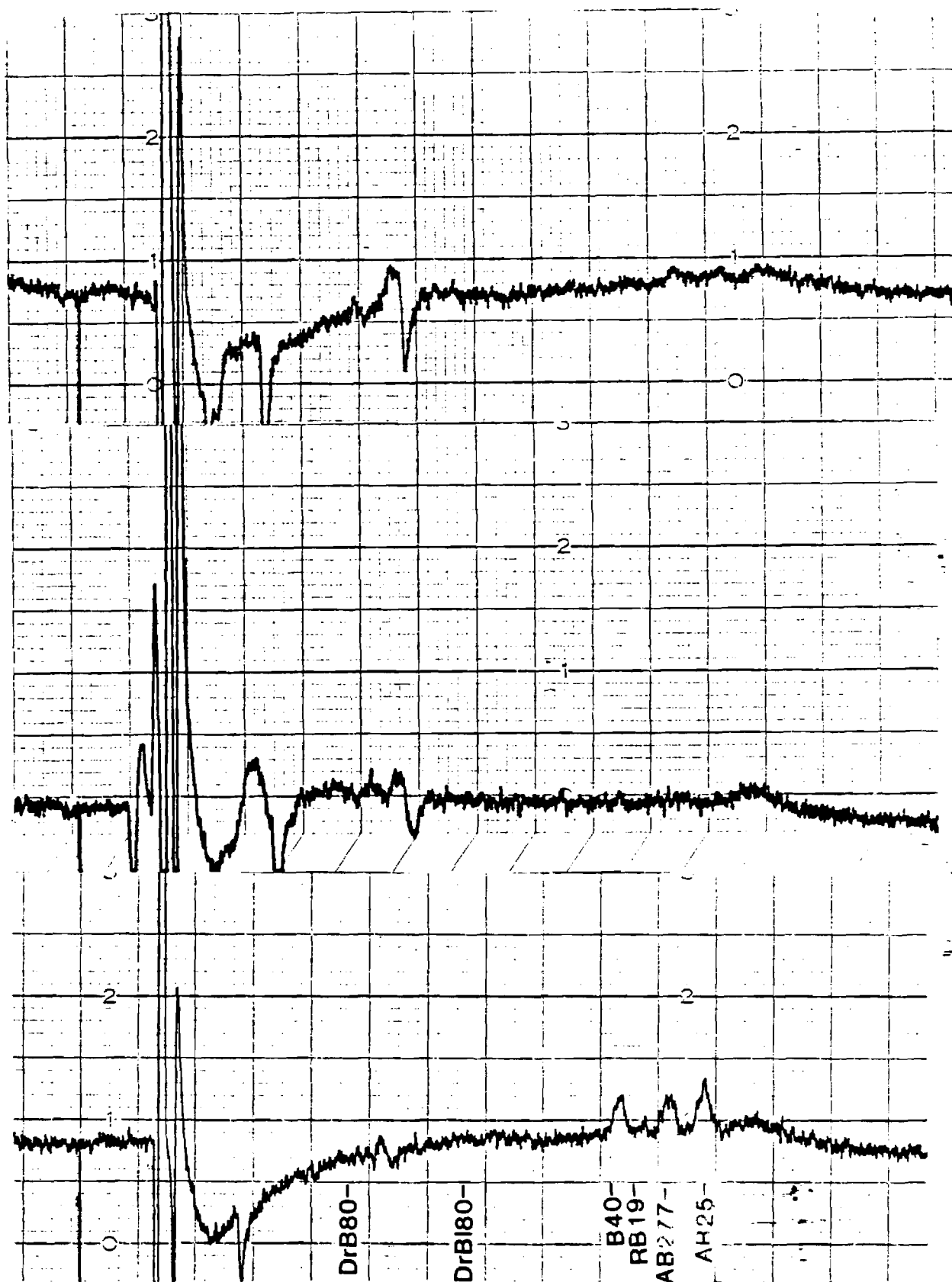


FIGURE 26 -- CHROMATOGRAMS OF COLUMN EFFLUENTS - CONTROL COLUMN (TOP) DYE COLUMN (MIDDLE) 0.5ppm STANDARD (BOTTOM) DIRECT, ACID AND REACTIVE BLUE DYES

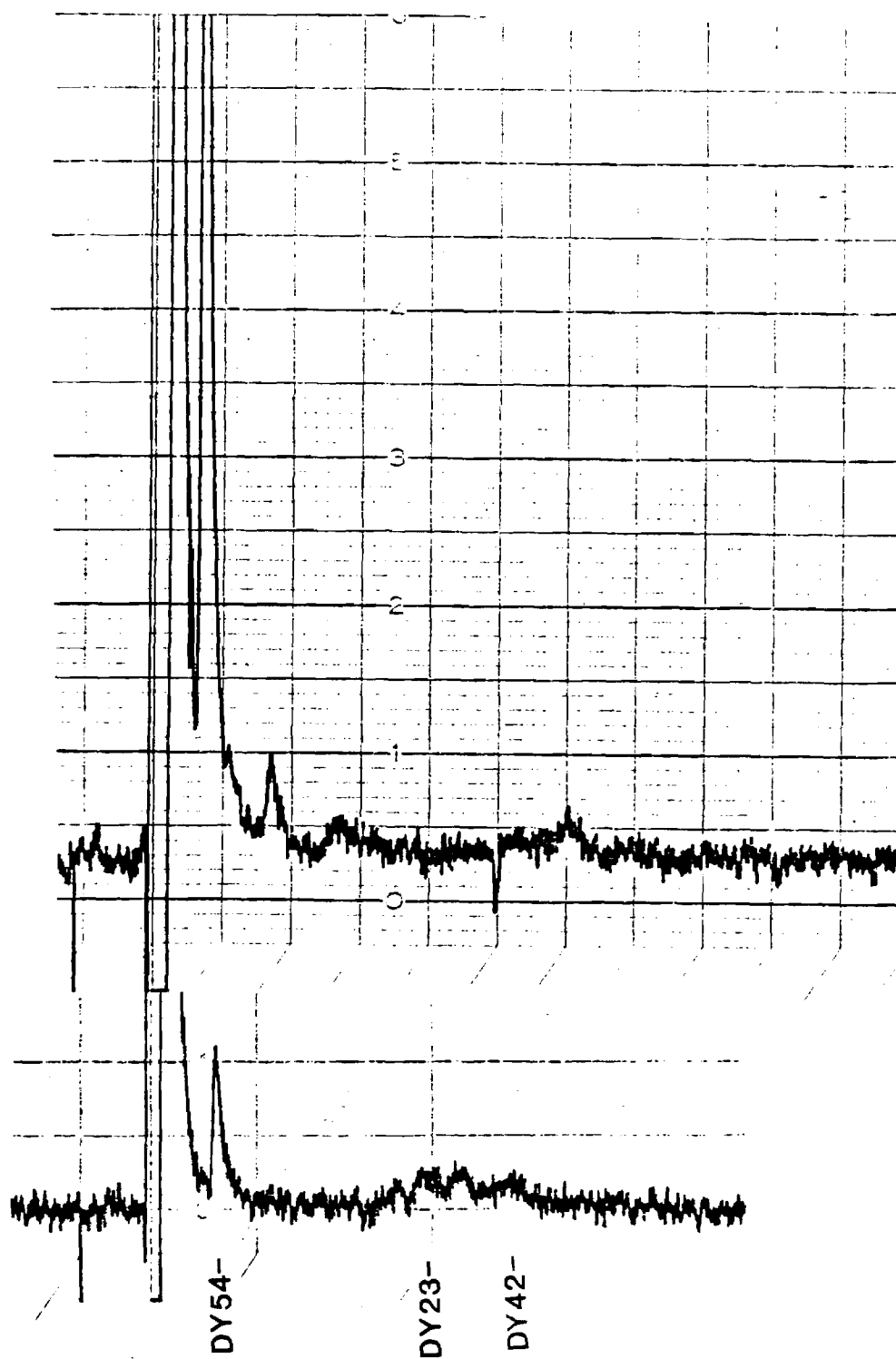


FIGURE 27 -- CHROMATOGRAMS OF DYE COLUMN INTERIOR (TOP) AND 0.5ppm  
STANDARD DISPERSE YELLOW DYES

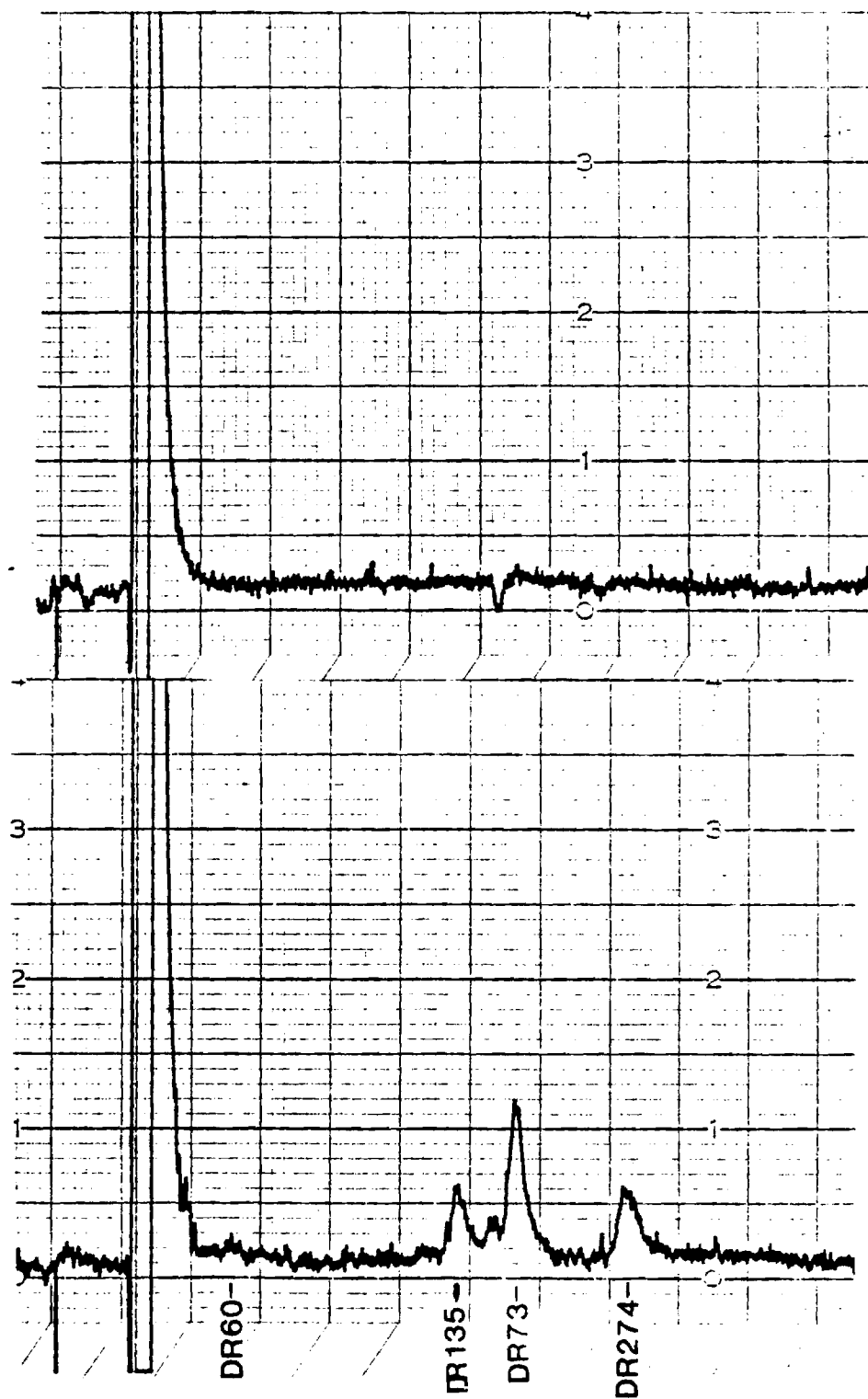


FIGURE 28 -- CHROMATOGRAMS OF THE DYE COLUMN INTERIOR (TOP)  
AND 0.5ppm STANDARD DISPERSE RED DYES

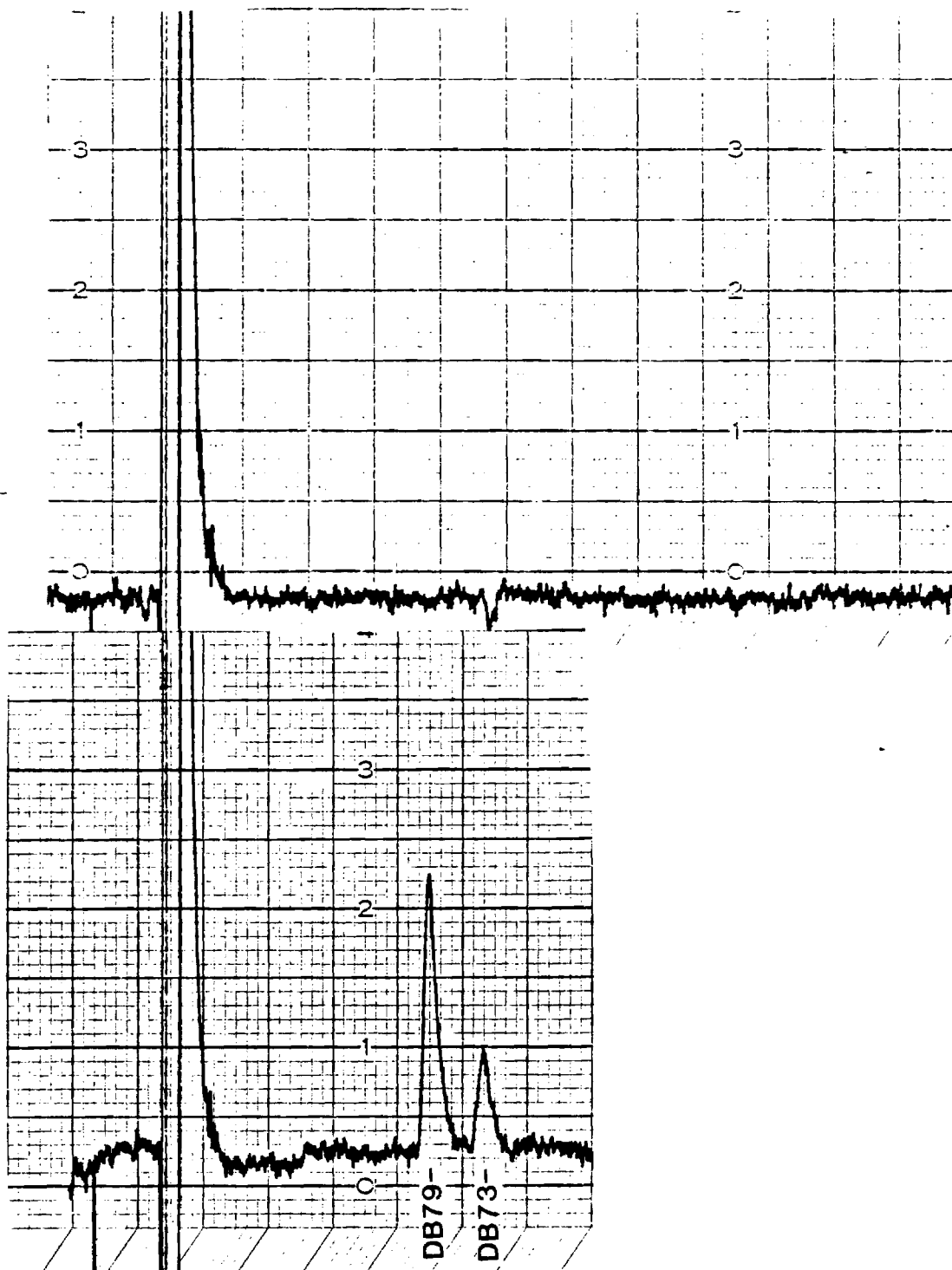


FIGURE 29 -- CHROMATOGRAM OF DYE COLUMN INTERIOR (TOP) AND 2ppm STANDARD SOLUTION OF DISPERSE BLUE DYES (BOTTOM)



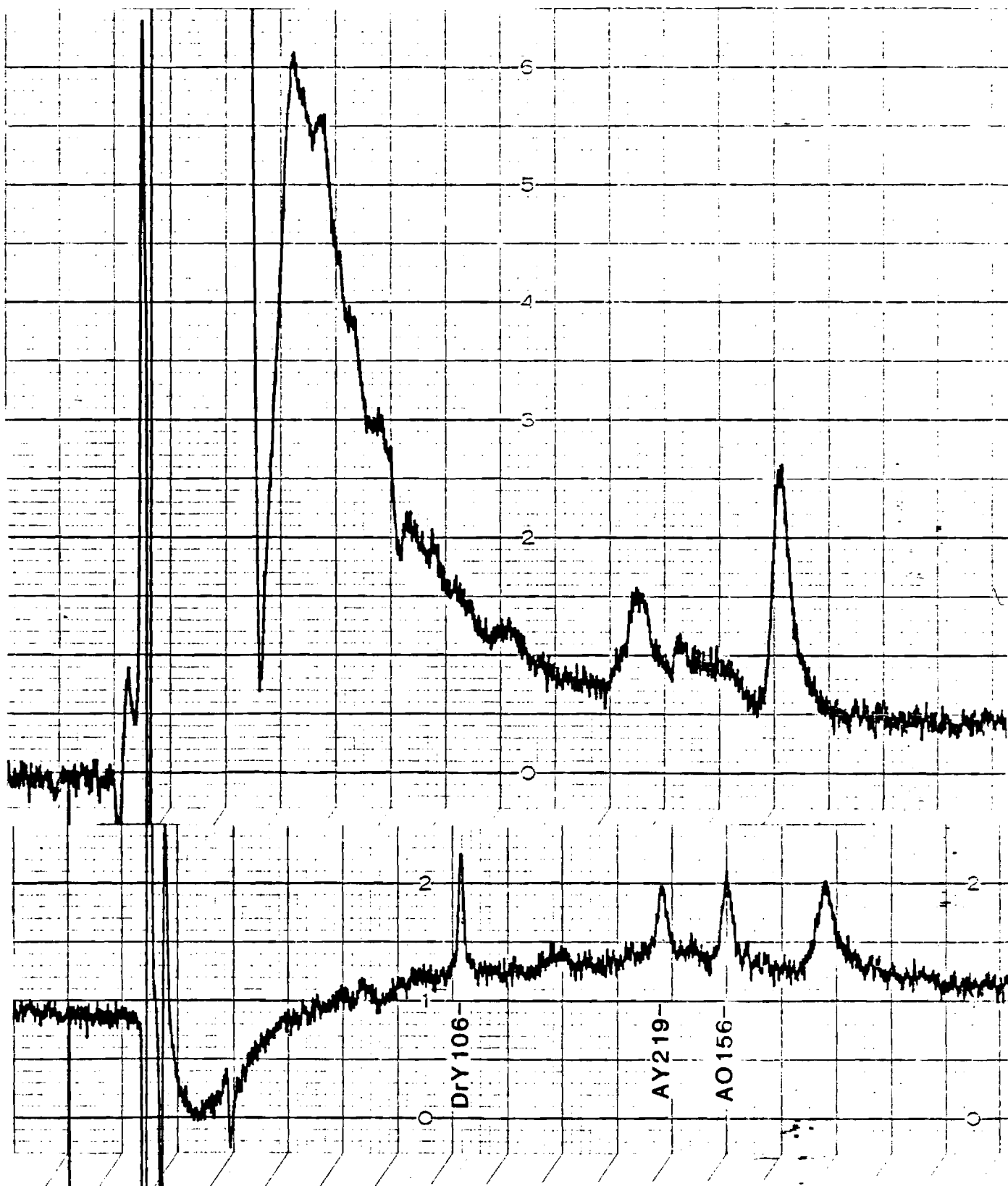


FIGURE 30 -- CHROMATOGRAM OF DYE COLUMN INTERIOR (TOP) AND 0.5ppm STANDARD SOLUTION OF DIRECT, ACID AND REACTIVE YELLOW DYES (BOTTOM)

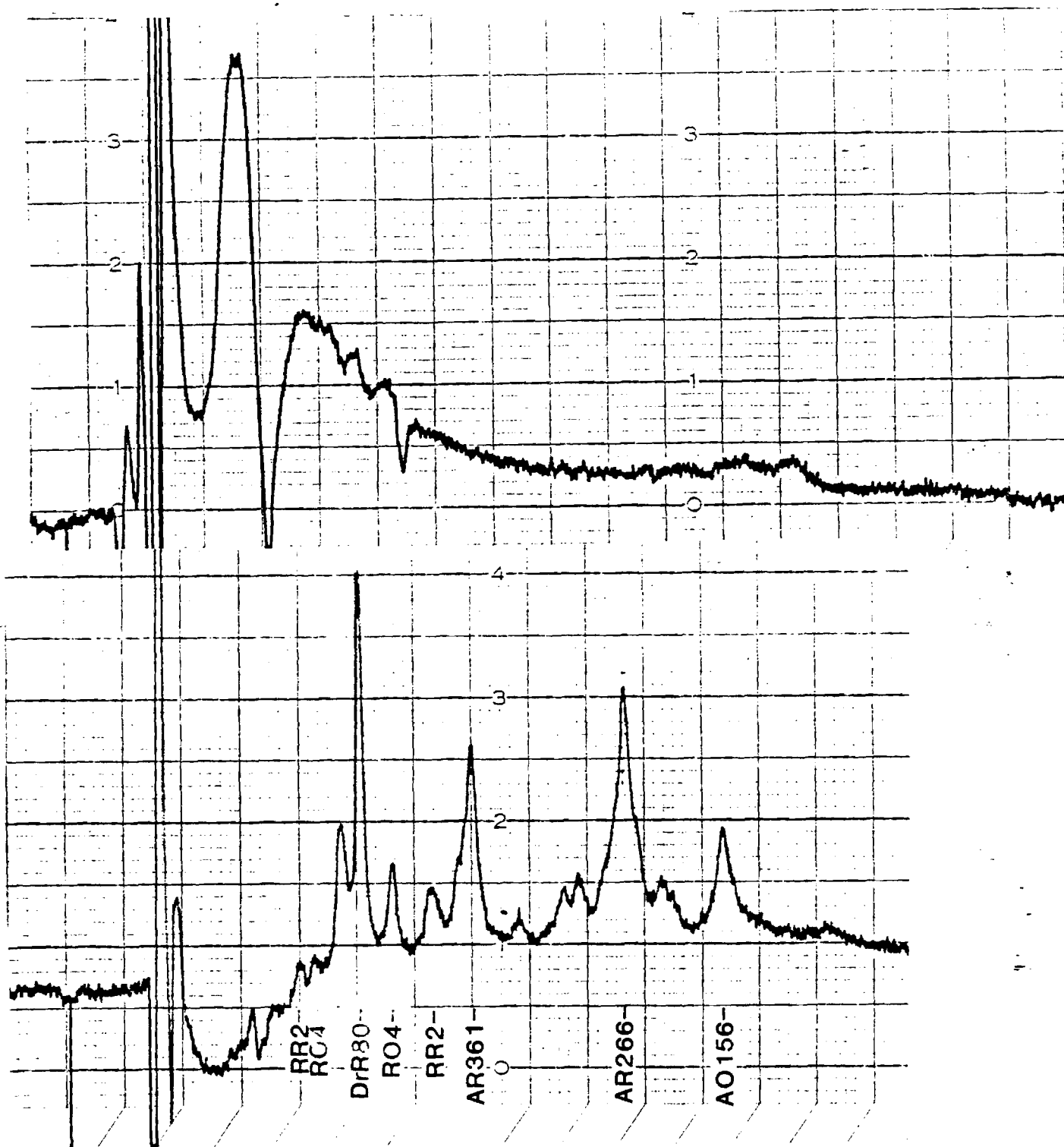


FIGURE 31 -- CHROMATOGRAMS OF DYE COLUMN INTERIOR (TOP) AND 3.0ppm<sup>±</sup> STANDARD SOLUTION OF DIRECT, ACID, AND REACTIVE RED DYES (BOTTOM)

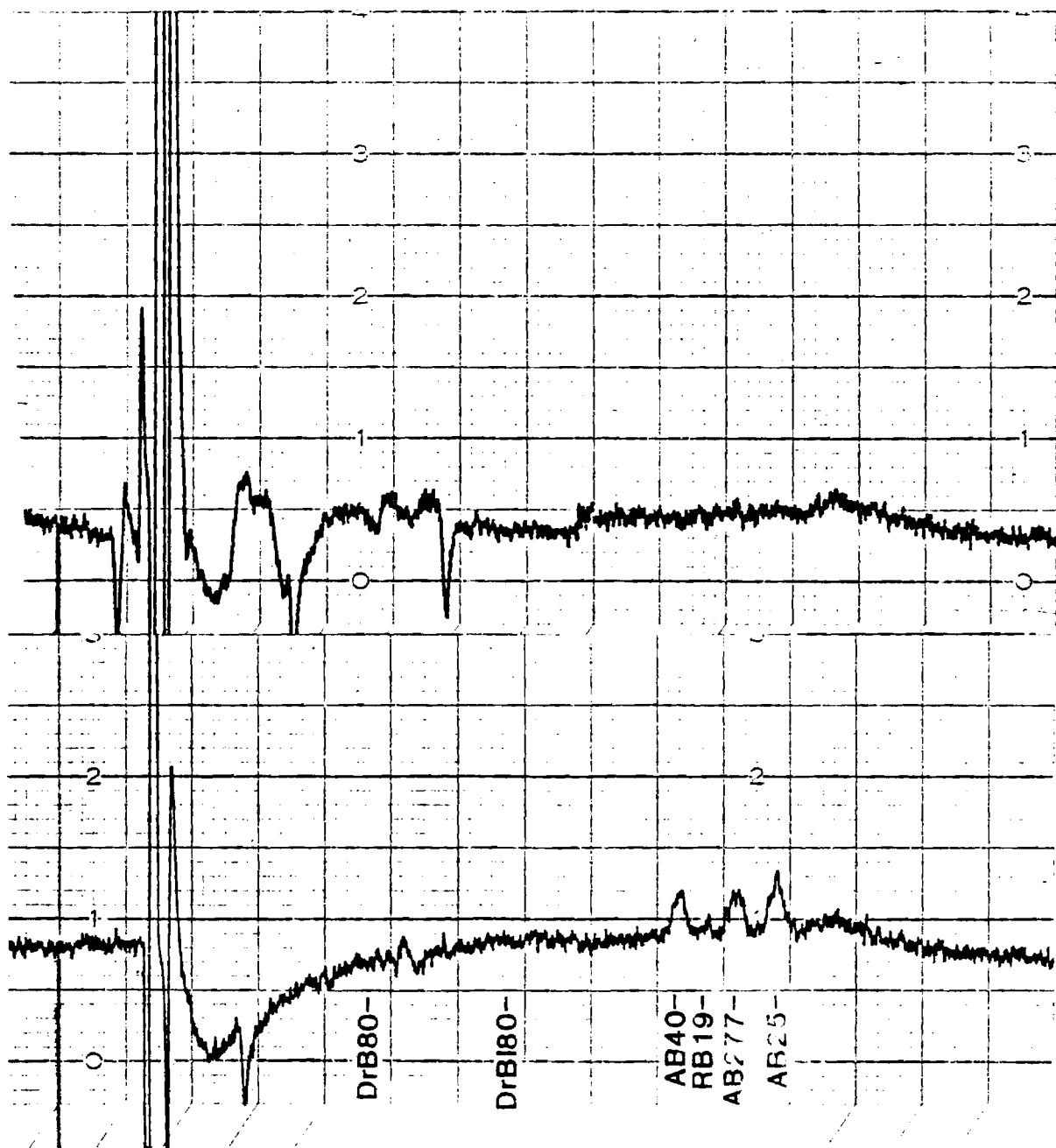


FIGURE 32 -- CHROMATOGRAMS OF DYE COLUMN INTERIOR (TOP) AND 0.5ppm STANDARD SOLUTION OF DIRECT, ACID AND REACTIVE BLUE DYES (BOTTOM)

## APPENDIX B

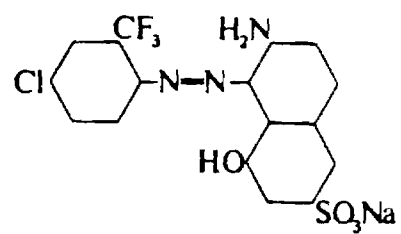
### PUBLISHED STRUCTURES OF DYES IN THIS STUDY

NOTE: The Colour Index convention of not depicting the aromatic nature of ring structures has been followed in this Appendix.

# ACID DYES

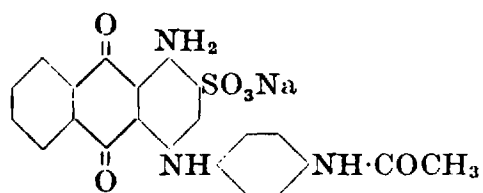
**C.I. 17101**

**C.I. Acid Red 266**



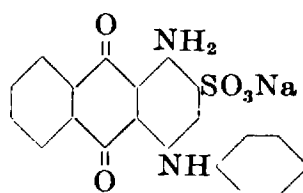
**62125**

**C.I. Acid Blue 40**



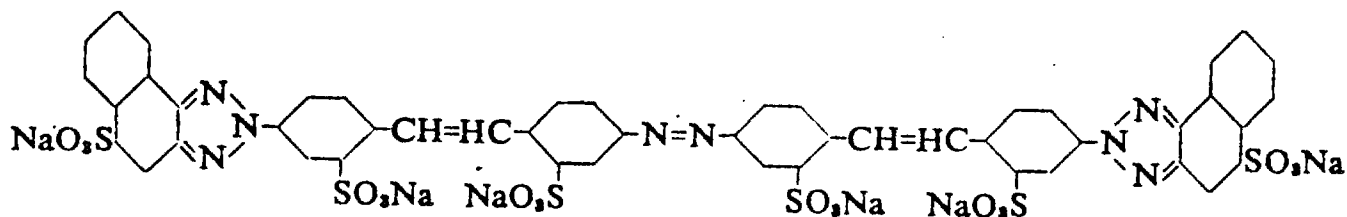
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**C.I. Acid Blue 25**

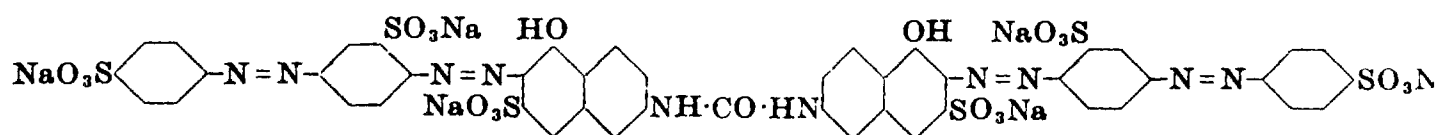


DIRECT DYES

**C.I. 40300      C.I. Direct Yellow 106**

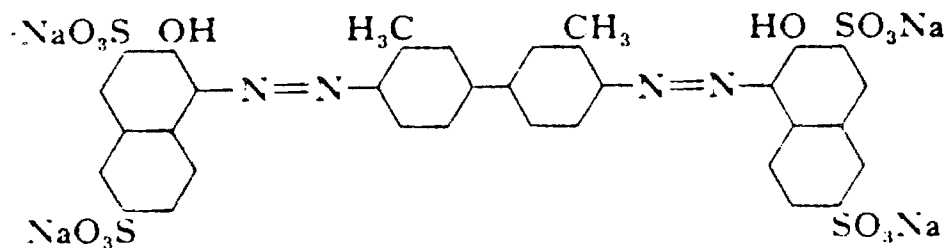


**35780      C.I. Direct Red 80**

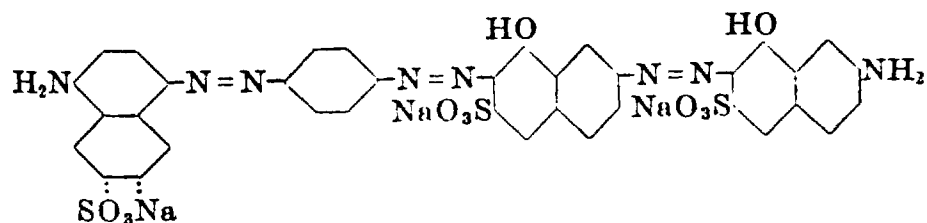


**24315      C.I. Direct Blue 80**

Bis copper complex, derived from

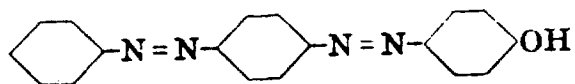


**31600      C.I. Direct Black 80**

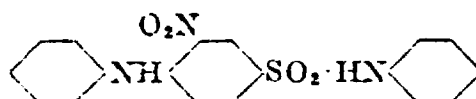


DISPERSE DYES

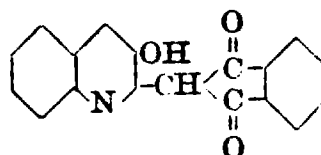
**26070★ Disperse Yellow 23**



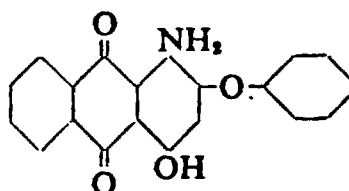
**10338 C.I. Disperse Yellow 42**



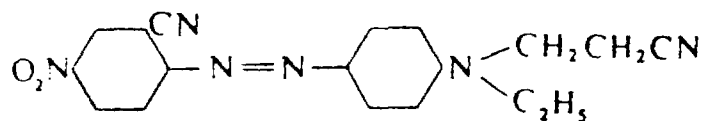
**47020★ C.I. Disperse Yellow 54**



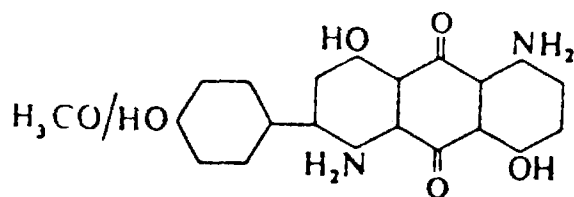
**C.I. 60756 C.I. Disperse Red 60**



**C.I. 11116 C.I. Disperse Red 73**



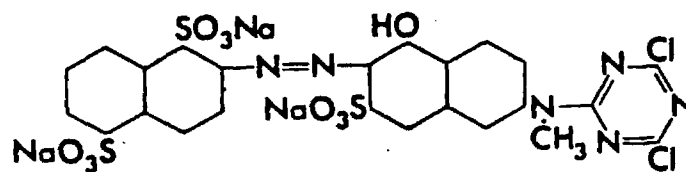
**C.I. 63265 C.I. Disperse Blue 73**



REACTIVE DYES

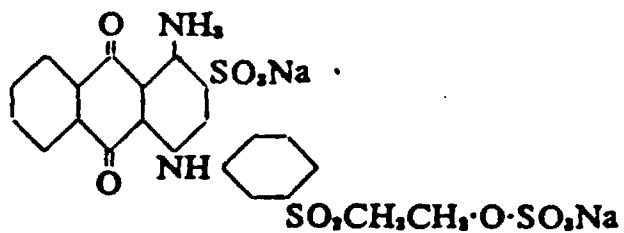
18260

C.I. Reactive Orange 4



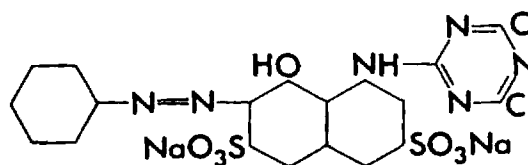
61200

C.I. Reactive Blue 19



C.I. 18200

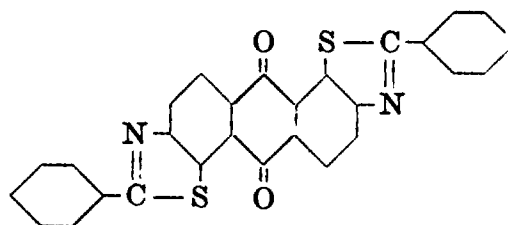
C.I. Reactive Red 2



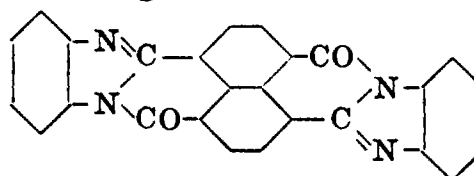


VAT DYES

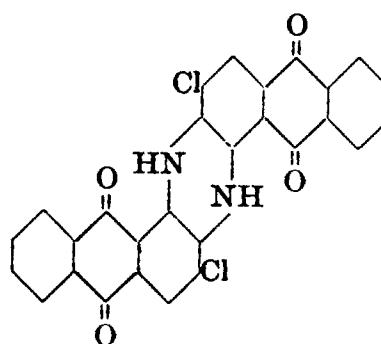
**67300 C.I. Vat Yellow 2**



**71105 C.I. Vat Orange 7**



**69825 C.I. Vat Blue 6**



APPENDIX C  
PRIORITY POLLUTANTS

## APPENDIX C

The Control Column Effluent, Dye Column Effluent and Dye Column Interior samples were analyzed by GC-MS for the following compounds on the EPA priority pollutants list.

Acenaphthene	Di-n-butylphthalate
Acenaphthylene	4,6-dinitro-2-methylphenol
Anthracene	2,4-Dinitrophenol
Benzo(a)anthracene	2,4-Dinitrotoluene
Benzo(b)fluoranthene	2,6-Dinitrotoluene
Benzo(k)fluoranthene	Di-n-Octylphthalate
Benzo(g,h,i)perylene	bis(2-Ethylhexyl)phthalate
Benzo(a)pyrene	Fluoranthene
4-Bromophenyl phenyl ether	Fluorene
Butyl benzyl phthlate	Hexachlorobenzene
bis(2-Chloroethoxy)methane	Hexachlorobutadiene
bis(2-Chloroethyl)ether	Hexachlorocyclopentadiene
bis(2-Chloroisopropyl)ether	Hexachloroethane
4-Chloro-3-methyl phenol	Indeno(1,2,3-cd)pyrene
2-Chloronaphthalene	Isophorone
2-Chlorophenol	Naphthalene
4-Chlorophenyl phenyl ether	Nitrobenzene
Chrysene	2-Nitrophenol
Dibenzo(a,h)anthracene	4-Nitrophenol
1,2-Dichlorobenzene	n-Nitrosodimethylamine
1,3-Dichlorobenzene	n-Nitrosodiphenylamine
1,4-Dichlorobenzene	n-Nitrosodi-n-propylamine
2,4-Dichlorophenol	Pentachlorophenol
Diethyl phthalate	Phenanthrene
2,4-Dimethylphenol	Phenol
Dimethyl phthalate	Pyrene
2,4,6-Trichlorophenol	1,2,4-Trichlorobenzene